

## Department of Energy Washington, DC 20545

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Mr. Gerry A. Harvey, Director Operations Support Services Westinghouse Hanford Company Post Office Box 1970 **Richland,** Washington 99352

Dear Mr. Harvey:

This Hazard and Operability Study (HAZOP) of the 300 Area Water Treatment Facility Chlorination System is a result of successful teamwork among the Department of <code>Energy</code> (DOE). Westinghouse Hanford <code>Company</code> (WHC), and <code>Battelle</code> staff members and <code>demonstrates</code> the-use and application of-a <code>major</code> process hazards analysis (<code>PrHA</code>) technique. The <code>PrHA</code> will support WHC chemical safety activities and provide a useful example for all <code>DOE</code> contractors.

In response to the requirements of the Process Safety Management of Highly Hazardous Chemicals (PSM) Rule (29 CFR 1910.119), DOE's Office of Safety and Quality Assurance established a PSM Program that provides guidance, training, and support to assist DOE contractors in their efforts to comply with the rule. As PrHA is considered a critical element of the rule, a demonstration analysis was planned as part of the program's 1993 work. When WHC operations personnel suggested an analysis be done of the 300 Area Water Treatment Facility Chlorination System, it seemed ideal for the demonstration. Chlorine is the most common chemical at DOE sites that is regulated under the PSM Rule and thus a demonstration analysis of a chlorination system would have wide applicability across DOE. The HAZOP technique was selected as it was judged appropriate to the complexity of the system and would effectively identify and evaluate the system's hazards.

This study is not only an example of a PrHA that we believe complies with the PSM Rule, but also demonstrates a structured, brainstorming technique that is a practical and effective management tool for the identification and control of hazards of any process. I would like to express my appreciation for the support of the WHC personnel whose participation made this study a success.

Si ncerel y,

Joseph E. Fitzgerald, Jr. Deputy Assistant Secretary Safety and Quality Assurance

CASTER WASTER

# **EXAMPLE PROCESS HAZARD ANALYSIS** OF A DEPARTMENT OF ENERGY **WATER CHLORINATION PROCESS**



September 1993

U.S. Department of Energy Assistant Secretary for Environment, Safety and Health Office of Deputy Assistant Secretary for Safety and Quality Assurance Washington, DC 20585

Comments or questions concerning this process hazard analysis or future technical assistance visits should be directed to:

## Sanjeeva Kanth, EH-31

270 CC U.S. Department of Energy Washington, DC 20585 301-903-4516 Fax: 301-903-8585

Express Mail Address: **EH-31**U.S. Department of Energy 19901 Germantown Road Germantown, MD 20874

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rigure C-5.	Liquid Chlorine Release from 1-inch Pipe Break

## LIST OF ACRONYMS

**AIChE** American Institute of Chemical Engineers

BLEVE boiling liquid expanding vapor explosion

CFR Code of Federal Regulations

DOE U.S. Department of Energy

HHC highly hazardous chemical

HAZMAT hazardous materials

HAZOP hazard and operability

IDLH immediately dangerous to life or health

MSDS Material Safety Data Sheet

ORPS Occurrence Reporting and Processing System

OSHA Occupational Safety and Health Administration

PrHA process hazard analysis

PNL Pacific Northwest Laboratory

ppm part per million

PSM process safety management

SCBA self-contained breathing apparatus

TQ threshold quantity

WAC Washington State Administrative Code

**WHC** Westinghouse Hanford Company

## EXAMPLE PROCESS HAZARD ANALYSIS OF A DEPARTMENT OF ENERGY WATER CHLORINATION PROCESS

### 1.0 INTRODUCTION

On February 24, 1992, the Occupational Safety and **Health** Administration (OSHA) released a revised version of Section 29 <u>Code of Federal Regulations</u> (<u>CFR</u>) Part 1910 that added Section 1910.119, entitled "Process Safety Management of Highly Hazardous Chemicals" (the PSM Rule). Because U.S. Department of Energy (DOE) Orders 5480.4 and 5483. 1A prescribe OSHA 29 <u>CFR</u> 1910 as a standard in DOE, the PSM Rule is mandatory in the DOE complex.

A major element in the PSM Rule is the process hazard analysis (PrHA), which is required for all chemical processes covered by the PSM Rule. The PrHA element of the PSM Rule requires the selection and application of appropriate hazard analysis methods to systematically identify hazards and potential accident scenarios associated with processes involving highly hazardous chemicals (HHCs).

The analysis in this report is an example PrHA performed to meet the requirements of the PSM Rule. The PrHA method used in this example is the hazard and operability (HAZOP) study, and the process studied is the new Hanford 300-Area Water Treatment Facility chlorination process, which is currently in the design stage. The HAZOP study was conducted on May 18-21, 1993, by a team from the Westinghouse Hanford Company (WHC), Battelle-Columbus, the DOE, and Pacific Northwest Laboratory (PNL). The chlorination process was chosen as the example process because it is common to many DOE sites, and because quantities of chlorine at those sites generally exceed the OSHA threshold quantities (TQs).

The report is organized into 13 sections and 5 appendices. Section 2.0 summarizes the requirements of the PSM Rule for performing PrHAs. Section 3.0 describes the scope and assumptions used in the analysis. Section 4.0 presents a list of recommendations and action items developed during the HAZOP study. Section 5.0 is an overview of the Hanford 300-Area Water Treatment Facility chlorination process, including process diagrams.

Section 6.0 contains brief descriptions of previous incidents at the Hanford 300-Area Water Treatment Facility involving the **old** chlorination process, and Section 7.0 summarizes the hazards of chlorine. Section 8.0 describes the HAZOP study method, and Section 9.0 lists the HAZOP team members and their roles.

Section 10.0 describes the location of the Hanford 300-Area Water Treatment Facility in relation to the public and to employees. Section 11.0 presents a brief discussion of the possible causes of human errors identified during the HAZOP study. The HAZOP summary is presented in Section 12.0, and Section 13.0 contains the study references.

Appendix A of this report contains the procedure for change-out of chlorine cylinders. The HAZOP study worksheets are provided in Appendix B. The effects of chlorine releases are estimated in Appendix C. Appendix D contains a Material Safety Data Sheet for chlorine. Appendix E presents the resumes of the HAZOP study team members.

## 2.0 SCOPE OF ANALYSIS

This report illustrates the use of the process hazard analysis (PrHA) required by the Occupational Safety and Health Administration (OSHA) rule 29 <u>CFR</u> 1910.119, "Process Safety Management of Highly Hazardous Chemicals" (the PSM Rule). The Hanford 300-Area Water Treatment Facility chlorination process was selected for analysis because it is a process common to many U.S. Department of Energy (DOE) sites, and quantities of chlorine at those sites generally exceed the OSHA threshold quantities (TQs). The analysis method selected was the hazard and operability (HAZOP) study.

The HAZOP study was performed on the new chlorination process design at the Hanford 300-Area Water Treatment Facility. At the time of the study, the new system was partially installed but not operating. The HAZOP study consisted of four full-day sessions and covered both the chlorination process and the procedures for change-out of chlorine cylinders. The worksheets in Appendix B document the HAZOP study.

The study assumed that the chlorination process was essential and that questions regarding elimination or replacement of chlorine with other types of disinfection technologies were outside of scope. Although a separate seismic analysis was not performed, seismic failures were considered similar to existing HAZOP study scenarios (e.g., line, valve, and cylinder failures).

Additional information regarding the PSM Rule and the performance of PrHAs is available in the *DOE Guideline: Preliminary Guide for Conformance with OSHA's Rule for Process Safety Management of Highly Hazardous Chemicals* (Draft, **DOE/EH**, March 1993), and the *DOE Guideline: Guide for Chemical Process Hazard Analysis* (Draft, **DOE/EH**, March 1993).

## 3. 0 PROCESS HAZARD ANALYSIS REQUIREMENTS

This section provides a general overview of the process safety management (PSM) requirements and objectives for conducting process hazard analyses (PrHAs) under the Occupational Safety and Health Administration (OSHA) rule 29 <u>CFR</u> 1910.119, the PSM Rule. This section would not normally be included in a PrHA. Rather, in its place would be a section discussing the specific objectives that management wished to accomplish in the PrHA.

## 3.1 Objectives

The objective of the PSM rule is to protect employees by preventing or minimizing the consequences and impacts of chemical accidents involving highly hazardous chemicals **(HHCs).** This objective is partly fulfilled by performance of PrHAs to identify hazards and recommend safety improvements in the design and operation of chemical processes. The scope and level of detail of a PrHA must be appropriate to the complexity of the chemical process being evaluated. A PrHA should

- Identify the hazards of a process
- Evaluate previous process incidents that had the potential to cause catastrophic consequences or impacts in the workplace
- Evaluate the engineering and/or administrative controls applicable to the process hazards and their interrelationships (e.g., detection methods for releases)
- Identify the consequences of failure of engineering and/or administrative controls
- Review facility siting issues
- Evaluate the importance of human factors on the likelihood and/or consequences of process accidents
- Evaluate qualitatively the range of possible safety and health effects on employees from failure of engineering and/or administrative controls
- Identify procedural or process safety improvements to better control process hazards.

### 3.2 Review Team

The PSM Rule requires that a PrHA be conducted by a team consisting of the following individuals:

- At least one member with expertise in engineering and process operations
- At least one member with experience and knowledge specific to the process being evaluated
- A team leader knowledgeable in the specific PrHA methodology being used.

### 3.3 **Schedule**

If facilities have more than one process covered by the PSM Rule, facility management must determine and document the priority order for conducting PrHAs for all the covered processes. The order for completing PrHAs should be based on a rationale that includes such considerations as

- The extent of the process hazard
- The number of potentially **affected** employees
- The age of the process
- The operating history of the process.

PrHAs for processes covered by the PSM Rule must be completed according to the following schedule:

- No less than 25 percent by May 26, 1994
- No less than 50 percent by May 26, 1995
- No less than 75 percent by May 26, 1996
- All of the initial PrHAs (100 percent) by May 26, 1997.

PrHAs completed after May 26, 1987, that meet the requirements of the PSM Rule are acceptable as initial PrHAs. They must be updated and **revalidated** in accordance with the PSM Rule requirements.

## 3.4 **Methodology**

The PrHA element of the **PSM** Rule requires the selection and application of appropriate hazard analysis methods to systematically identify hazards and related accident scenarios associated with highly hazardous chemicals. Although the PSM Rule allows the use of several different methods, it requires that the selection of a particular method be based on consideration of the process **being** analyzed. One or more of the following methods, or

an appropriate **equivalent** method, must be used: what-if study, checklist, what-if/checklist, HAZOP study, **failure** mode and effects analysis, and/or fault tree analysis.

## 3.5 **Recommendations and Updates**

The resolution of PrHA findings and recommendations are not part of a PrHA, *per se.* However, an employer must establish a system to promptly address a PrHA team's findings and recommendations. A schedule for resolutions must be established to assure that all recommendations are resolved and documented. All actions taken as a result of PrHA findings must be completed as soon as possible and must be reported to employees involved in the process and to any other individuals affected by the recommendations or actions.

Every 5 years the PrHA must be updated to ensure it is consistent with the current process, configuration, and operation. The PrHA, related updates, and the documented resolution of the recommendations are required to be maintained for the life of the process.

## 4.0 SUMMARY OF RECOMMENDATIONS

**The** action items and recommendations developed by the process hazard analysis **(PrHA)** team during the hazard and operability **(HAZOP)** study are presented in Table 1. The HAZOP study worksheets from which these action items and recommendations were derived are included in Appendix B.

Action items are typically assigned to specific individuals who are named in the "Responsibility" column in the matrix. However, because this report is an example **PrHA**, this column is left blank.

**Table 1. HAZOP Study Action Items** 

ACTION ITEM	SCENARIO	ACTION	RESPONSIBILITY
1	1-4	Check on the possibility of <b>backflow</b> past the rate indicator ( <b>rotameter</b> ) and adjust the procedures as needed.	
2	1-9, 3-1	Consider adding a procedure to verify that the vacuum can be maintained after the system is shut down to test for system leak tightness. This procedure should be used when the chlorinators are switched each month and whenever the polyethylene chlorine gas feed tubing is replaced.	
3	1-13	Verify that staff in adjacent buildings have received information on chlorine in their hazard communication (HAZCOM) program.	
4	2-5	Calculate possible temperatures (based on heat input versus heat loss) inside the chlorine cylinder storage facility if the heater thermostat fails "on" during peak outside temperatures. Base further action items on the results. Other key equipment affected by excessive temperatures should be considered. See the high-temperature alarm failure incident in Section 6.0.	
5	2-8	Check pressure potential from the chlorine cylinder and the system (regulator) response.  Determine whether the fusible plug will open with high pressure.	

**Table 1. HAZOP Study Action Items (Continued)** 

ACTION ITEM	SCENARIO	ACTION	RESPONSIBILITY
6	2-10, 2-11	Check with the vendor regarding possible entry of material other than chlorine into the chlorine cylinder or the possibility of complete substitution of another chemical that uses the same size container.	
7	3-2	Contact the vendor to determine the failure experience of the regulator failing "open" from wear, corrosion, dirt, or water. If the regulator has a relatively high probability of failing, controls (e.g., a remotely operated shutoff at the chlorine cylinder and failsafe action upon power loss) should be considered.	
8	3-10	Verify that the screens are in place on the regulator vents.	
9	4-4	The explanation of how the differential pressure regulator operates is missing from the vendor's documentation. This information should be obtained. <b>The</b> operation of the valve should be checked, and the potential for a pressure deviation should be assessed.	
10	4-13	Verify that monthly preventative maintenance includes checking the battery backup for the chlorine alarm.	
11	5-24	Ensure that the intent to incorporate the existing identification tagging into the disconnect procedures is completed.	
12	6-16	Consult the vendor about what the expected system response would be if the serviceman did not properly vertically align the chlorine tank (drawing liquid to the ejector). Determine the potential amount of chlorine that could be released.	

### 5.0 PROCESS DESCRIPTION

The Hanford 300-Area Water Treatment Facility uses gaseous chlorine to disinfect the drinking water supply at the Hanford Site 300-Area in accordance with the Washington State Administrative Codes (WAC) 246-290. Two independent chlorination systems are installed at the Water Treatment Facility. These systems can be operated separately or in parallel. Because they are typically operated separately, this study addresses only one system. Figures 1 through 4 are simplified diagrams of the chlorination process. Figures 5 through 8 are photographs of the chlorine cylinder storage area and the chlorination room. The chlorination system was partially installed and not yet operating at the time of the hazard and operability (HAZOP) study.

Within the chlorine cylinder storage area of the Water Treatment Facility, liquid chlorine is stored in two 1-ton cylinders (see Figures 6, 7, and 8). One cylinder is normally in service, and the other is in standby mode for use when the contents of the in-service cylinder are depleted.

Chlorine leak detection and warning are provided by two sets of alarms. The alarms sound locally at the Water Treatment Facility and remotely at a separate facility that is staffed 24 hours a day. One alarm indicates a chlorine concentration of 1.0 part per million (ppm) and is used to detect a slow buildup of chlorine. A second alarm, set at 5.0 ppm, is used to detect larger chlorine releases. The chlorine cylinder storage area is also equipped with a manually activated exhaust vent system to evacuate chlorine before personnel entry.

Chlorine cylinders are placed on trunnions and dollies to move them in and out of the storage area (see Figure 6). The dollies operate on fixed tracks with "stops" to prevent them from traveling too far. Wheel chocks prevent movement of the dollies while the chlorine cylinders are in use.

Two gaseous chlorinators are installed in a separate room adjacent to the chlorine cylinder storage area. The chlorinators meter and inject gaseous chlorine into the raw water supply as it enters the Water Treatment Facility sedimentation basins. The chlorination room is equipped with an exhaust vent fan and chlorine leak detection system. The leak detector is equipped with alarm capabilities that alarm both locally and remotely at a separate facility that is staffed 24 hours a day.

Chlorine gas is supplied from the in-service chlorine cylinder at approximately 75 psig to a vacuum regulator mounted directly to the cylinder gas supply valve. An automated switch-over valve is installed between the containers to allow both containers to be connected to the in-use chlorinator at the same time. As one container approaches depletion, a sensor detects the high-vacuum condition causing the valve to switch to the standby container. The vacuum regulator reduces the pressure from the cylinder by using a water ejector to create a vacuum within the system. The regulator is designed to fail "closed" any time a loss of vacuum is experienced within any component of the system. The regulator is also designed to relieve the pressure from the system.

Gaseous chlorine is drawn through a flow rate indicator/controller, an automatic control valve, and a differential pressure regulator, to a water ejector. The chlorine rate indicator is set manually to maintain a **feed** rate of 20 to 60 pounds per day. Feed rate depends on ambient weather conditions and the quantity of water processed. Chlorine gas is mixed with water from the clear-well as the gas passes into the water **stream** at the water ejector. The chlorinated water is then discharged into the raw water supply at the influent chamber, where initial treatment of the water supply begins. The water undergoes sedimentation and filtering (rapid sand filters) before entering the 70,000-gallon clear-well reservoir.

The water system is monitored during each shift for residual chlorine. Monitoring occurs at the clear-well and at various **facilities** throughout the Hanford **300-Area** to assure that the proper amount of chlorine is present to effectively disinfect the water supply. Depending on the results of the monitoring, the chlorine **feed** rate is manually adjusted to maintain sufficient chlorine for disinfection.

Chlorine cylinders are delivered to the chlorine cylinder storage building on flat bed trucks as needed. The cylinders are loaded and unloaded from the truck using a mobile crane. Hoisting and rigging crews are trained to perform the loading and unloading activities.

In **case** of system outages, a water line from the City of **Richland** can temporarily supply water to the Hanford 300-Area.

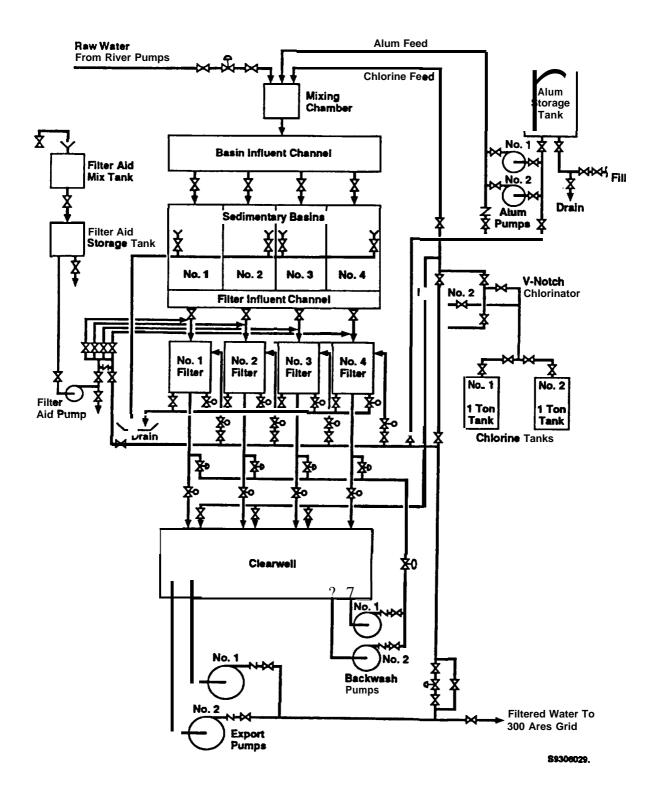
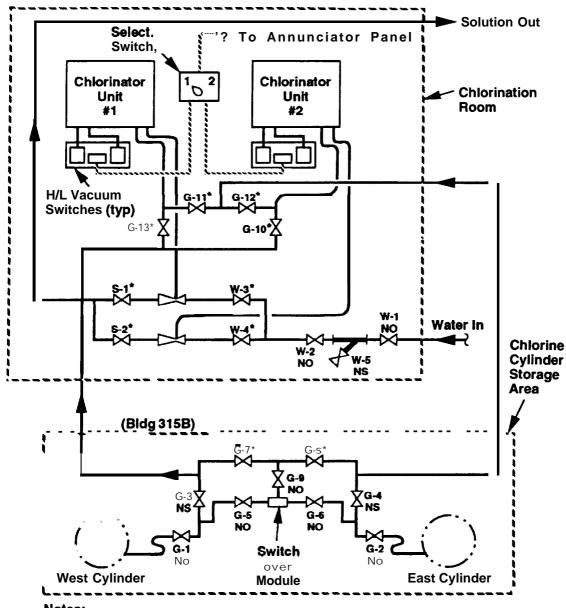


Figure 1. Process Flow Diagram of the Hanford 300-Area Water Treatment Facility



### Notes:

- Position depends on which chlorinator or cylinder and/or chloine supply iine is in-service
- NO Normally open NS Normally shut

39306007.1A

Figure 2. Chlorination Process Flow Diagram, Water Treatment Facility

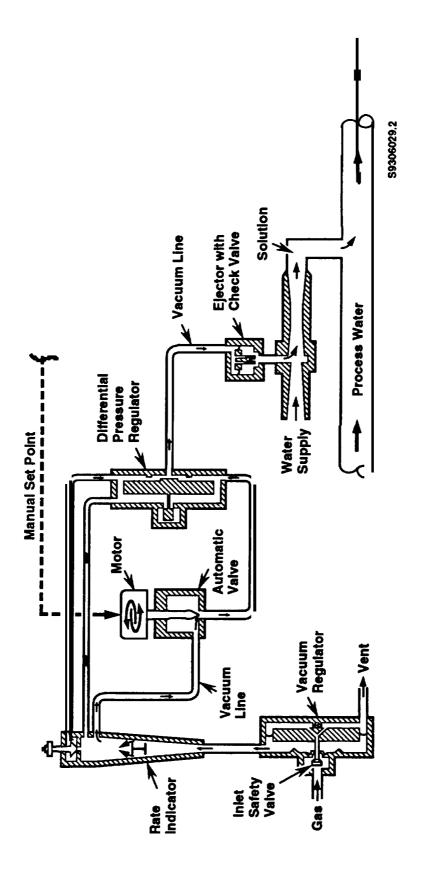
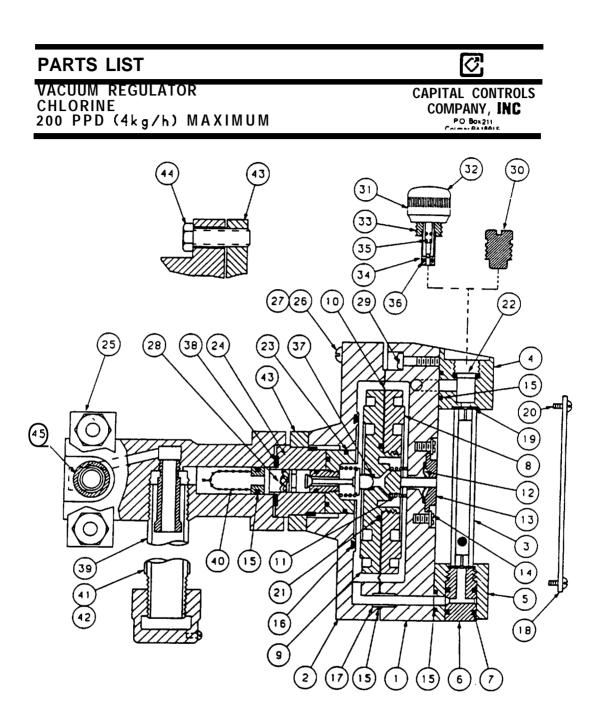


Figure 3. Automatic Gas Feed System, Chlorination Process



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Figure 4. Vacuum Regulator, Automatic Gas Feed System

ITEM NO.	OTY.	D ESCRIPTION	PART NO.	ITEM NO.	QTY.	DESCRIPTION	PART NO.
1	1	FRONT BODY	SEE CHART IV	26	2	SCREW, 1 /4-20 X 2-3/4 LG	N-125
2	1	BACK BOOY	U-160	27	6	SCREW, 1 /4-20 X 1 -3/4 LG	N-124
• 3	1	FLOWMETER ASSEMBLY	SEE CHART I	+ 28	1	REPLACEMENT FILTER ISEE NOTE 6)	I3M-1023
4	1	FLOWMETER TOP FITTING	M-117	29	4	SCREW, 10-24 X 1 LG	N-128
6	1	FLOWMETER BOTTOM FITTING	M-1 16	30	i	BONNET PLUG	M-176
+ 6	1	METER INLET PLUG	U-140	31	1	RATE VALVE ASSEMBLY	SEE NOTE 3
+ 7	2	O-RING	OV-11-112	32	1	VALVE STEM ASSEMBLY	SEE CHART I
+ 8	1	DIAPHRAGM FRONT PLATE	U-269	33	i	VALVE BONNET	V- 124
+ 9	1	DIAPHRAGM BACK PLATE	A-363	34	1	VALVE SLEEVE	SEE CHART I
+ 10	1 SET	DIAPHRAGM (2 PER SETI	0-106	+ 36	2	O-RING	OV-11-006
11	1	RELIEF SPRING	s-loo	+ 36	1	O-RING	0V-11-010
+ 12	1	SEALING DIAPHRAGM	D- 102	+ 37	1	O-RING	Ov-11 <b>-009</b>
13	1	SEAL COVER	U-137-1	+ 38	1	LEAD GASKET (SEE NOTE 6)	G-ill
14	2	SCREW, 10-24 X 3/16 LG	N-128	3s	1	INLET ASSEMBLY	SEE CHART III
+ 16	4	D-RING	0V-11-012	+ 40	1	INLET FILTER ASSEMBLY	BM-1276
+ 16	1	O-RING	QV-1 1-332	" 41	1	HEATER	SEE CHARTII
+ 17	1	FLOW TUBE	U-182	+ 42	2	MOUNTING CUP	T-468
18	1	FRONT PLATE	R-2204	43	1	BODY PLATE	T-1 163-1
" 19	2	METER GASKET	SEE CHART I	44	2	BOLT. <b>HEX 3/8-16</b> X 1 LG	N-139
20	2	SCREW, 6-32 X 1/4 LG	N-302	46	1	LEAD GASKET (SEE NOTE 5)	SEE CHART III
+ 21	1	O-RING	OV-1 1428	l NS	1	3/8 TUBING CONNECTOR (VENT)	F-loo
+ 22	1	O-RING	OV-11-110	+ N/S	1	1/2 TUBING CONNECTOR (VACUUM)	F-106
+ 23	1	O-RING (SEE NOTE 6)	QV-11-212	I			
+ 24	1	INLET CAPSULE ASSEMBLY	BM-4869	N/s - NOT S	HOWN		
26	1	YOKE ASSEMBLY ISEE NOTE 4)	SEE CHART III				

#### CHART I

ITEM		CAPACITY	IN PPD (KG/H)	
NO.	25 (0.5)	50 (1.0)	100 (2.0)	200 (4.0)
3	A-108-6	A-108-6	A-108-8	A-108-9
19	G-100-8	G-100-7	G-100-7	G-100-4
31	BM-11 8-3	BM-1 18-3	BM-11 B-3	BM-11S-4
32	A-869-3	A-859-3	A-859-3	A-859-4
34	V-1 26-3	V- 126-3	v-126-3	V-126-4

#### CHART II

ITEM	VOL	TAGE
NO.	120 VAC 25 WATT	240 VAC 25 WATT
41	R-iII	R-260

#### CHART III

ITEM		CONNECTIONS	
NO.	U.S. LEFT HAND	U.S. RIGHT HAND	JAPAN
26	A-126	A-128	A-826
39	A-738-L	A-738-R	BM-1 160
46	G-ill	0-111	G-120

#### CHART IV

ITEM	WITH LOSS OF	WITHOUT LOB3
NO.	GAS SWITCH	OF GAS SWITCH
1	SEE P/L B3.7 133	

### NOTES:

- 1. (+) AND (\*) INDICATES RECOMMEND ED AS MINIMUM SPARE PARTS. QUANTITY
  RECOMMENDATIONS ARE FOR AVERAGEUSE AND CONDITIONS. ADDITIONAL PARTS
  AND QUANTITIES SHOULD BE CONSIDERED WHERE THE EQUIPMENT IS USED TO ITS
  FULLEST CAPABILITY OR WERE LOCATED IN AN AREA REMOTE FROM CONVENIENT
  SERVICE.
  - (A) TO ORDER RECOMMENDED SPARE PARTS INDICATED BY (+) SPECIFY BM-3269.
  - (B) TO ORDER RECOMMENDED SPARE PARTS INDICATED BY 1")
    SPECIFY INDIVIDUAL PARTS.
- WHEN ORDERING PARTS, SPECIFY GAS FEEDER CAPACITY, MODEL NUMBER, AND SERIAL NUMBER.
- ITEM NO. 31 INCLUDES ITEM NOS. 22, 32, 33, 34, 36, AND 36. TO ORDER COMPLETE RATE VALVE ASSEMBLY BEE CHART L
- 4. ITEM 26 YOKE ASSEMBLY IS INCLUDED IN ITEM 39 INLET ASSEMBLY.
- 6. TO ORDER TWELVE (121 GASKETS SPECIFY THE FOLLOWING:

FOR G-1 11 SPECIFY BM-918

FOR G-120 SPECIFY BM-919.

6. ITEM 23 O-RING AND ITEM 28 FILTER INCLUDED IN ITEM 24 INLET ASSEMBLY.

Figure 4. Vacuum Regulator, Automatic Gas Feed System (continued)

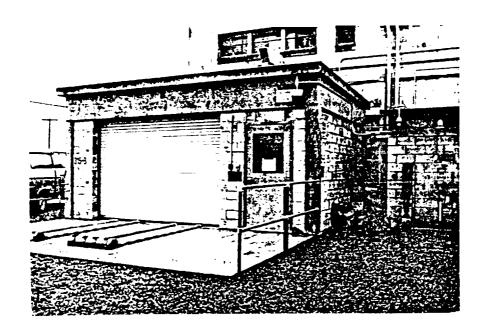


Figure 5. Building Housing Chlorine Cylinders and Chlorination Process Equipment

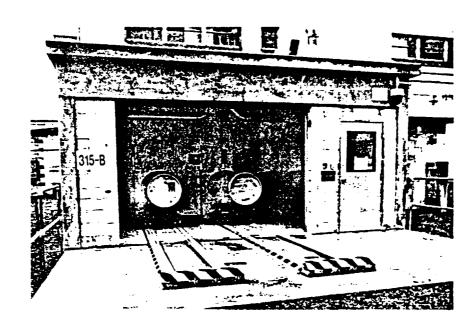


Figure 6. Chlorine Cylinder Storage and Change-out Area, Overhead Door Open

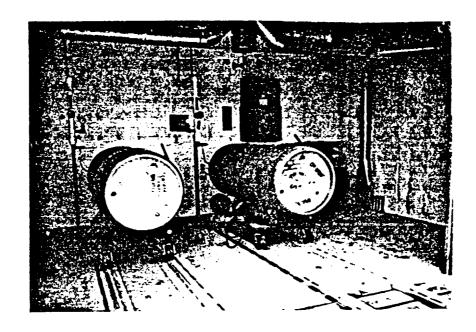


Figure 7. Chlorine Cylinders in the Chlorine Cylinder Storage Area, Front View

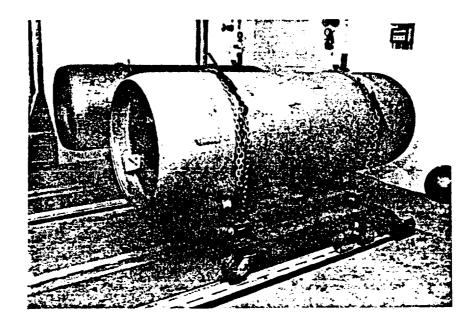


Figure 8. Chlorine Cylinders in the Chlorine Cylinder Storage Area, Side View

## 6.0 REVIEW OF PREVIOUS INCIDENTS

The following incidents involved the former chlorination system for the Hanford 300-Area Water Treatment Facility. Information about these incidents was obtained from the U.S. Department of Energy (DOE) Occurrence Reporting and Processing System (ORPS). Where relevant, these incidents were considered during the hazard and operability (HAZOP) study for the new system.

- 10/9/92 **Leak Detector Failure The** leak detector was outside of specified tolerances, as required in the maintenance procedure. Plant operations personnel were notified. Replacement parts were not available, and the maintenance craftsman removed the device from service until parts could be obtained the next day. During the swing and the following day shift, personnel did not know the detector had been removed from service. A "conduct of operations" review of the day's activities was held with **all** on-coming and off-going **staff**. This leak detector had experienced recurring failures and was replaced. (See Scenario 5-2 in the HAZOP study worksheets, Appendix B.)
- 11/19/92 Chlorine Leak The chlorine detector in the chlorination room alarmed in the afternoon, indicating that one of the chlorinators was leaking. Facility operations personnel were evacuated, and the Hanford Fire Department Emergency Response Team was notified. The system was shut down, the in-service chlorinator was isolated, and the standby chlorinator was put into service. No one was injured, and only a minimal amount of chlorine was released. The chlorine was generally confined to the chlorination room. It was determined that the #1 chlorinator injector system had developed a leak. The system tiled because of imperfections within gasket material. The failed material was replaced. (See Scenarios 1-4, 1-10, and 4-9 in the HAZOP study worksheets, Appendix B.)
- 11/21/92 Chlorine Leak A chlorine alarm was received, the Hanford Fire Department was notified, and the Hanford Hazardous Materials (HAZMAT) Team was dispatched. The Hanford 300-Area Water Treatment Facility was shut down. A tie-in line was put into service to supply water to the Hanford 300-Area from the City of Richland after Richland was notified. Failed internal parts of the #2 chlorinator and a system isolation valve packing gland were leaking. A weak spring in a chlorinator pressure-regulating valve caused a rubber diaphragm to fail. There were no injuries, and the minimal amount of chlorine released was generally confined to the chlorination room. The spring and diaphragm were replaced. The isolation valve was repacked. (See Scenarios 1-10 and 1-4 in the HAZOP study worksheets, Appendix B.)
- 1/4/93 Chlorine Leak Detector Alarm While performing routine equipment changes, the onduty operator noticed a chlorine odor in the chlorination room. After the operator exited, the chlorine leak detector in the building alarmed. The plant operator evacuated the Water Treatment Facility, and the Hanford HAZMAT

Team responded and isolated the system. The Water Treatment Facility was shut down, and the City of **Richland** water supply was **placed** in service. There were no injuries from the occurrence.

During maintenance activity, the operator had isolated and drained the in-service chlorinator according to procedures in effect at the time. These procedures did not allow sufficient time for evacuating the chlorine ejector prior to draining the chlorinator. The system was checked for leaks, but no leaks were found. The procedure was revised to allow sufficient time to evacuate the system. With different procedures now in place, this incident has consequences similar to Scenario 1-11 in the HAZOP study worksheets (see Appendix B).

• 1/16/93 Chlorine Leak **Detection Alarm** — A chlorine high-level alarm occurred. The Hanford Fire Department was notified, and several surrounding buildings were evacuated. Testing by the Hanford HAZMAT Team found no detectable chlorine in the air. Fewer than two hours later, the "all clear" was given. It was determined that the detector provided a **false** alarm. Tests performed by an instrument technician, however, showed that the detector was operating within the manufacturer's recommended tolerances. No leaks were identified when the system was restored to operation.

Prior to the occurrence, re-liquefaction of the gaseous chlorine within the chlorination room piping had been occurring. An additional heat source had been provided to **rectify** the problem. The heater had been placed next to the leak detector. The detector's electronics were **affected** by the increased room temperature. A voltage spike was created within the instrument and resulted in the **false** alarm. (See Scenarios 5-2 and 2-5 in the HAZOP study worksheets, Appendix B, and recommendation #4 in Section 4.0.)

### 7.0 IDENTIFIED HAZARDS

Chlorine has been used for many years to treat water on the Hanford Site. Westinghouse Hanford Company uses the Chlorine *Manual* (The Chlorine Institute, 1986, 5th edition), *Operating Procedure: Chlorine Cylinder Handling and Storage* (Westinghouse Hanford Company, no date), and the *Material Safety Data Sheet* (MSDS) (Occupational Health Services, Inc., 1993; see Appendix D) as references for chlorine handling.

## 7.1 Properties of Chlorine

Chlorine is a dense, nonflammable, greenish-yellow gas with a **bleach-like** choking odor. It is **2.5** times heavier than air. Liquid chlorine is a clear amber color and is 1.5 times heavier than water. Chlorine is generally shipped as a compressed, **liquified** gas with a vapor pressure of **85.5** psig at **70°F**. In both gaseous and liquid states, chlorine is nonflammable and nonexplosive. However, like oxygen, it is capable of supporting the combustion of substances such as hydrogen, ammonia, fuel gases, ether, turpentine, and most hydrocarbons. Finely divided metals and organic matter may react violently with chlorine. Steel and iron ignite and bum in an atmosphere of chlorine at about **484°F**. Chlorine reacts with water to form corrosive solutions of hydrochloric and **hypochlorous** acid.

## 7.2 Physiological **Effects**

Chlorine is corrosive, highly toxic, and severely irritating to all living tissue. Exposure may cause skin bums, permanent eye damage, and damage to the respiratory system. Inhalation exposure to higher **concentrations** of chlorine may be fatal. Airborne concentrations of chlorine above 3 to 5 parts per million **(ppm)** by volume are readily detectable by a normal person. In higher concentrations, the irritating effect of chlorine makes it unlikely that any person would willingly remain in a chlorine-contaminated atmosphere.

Persons exposed to airborne concentrations of chlorine greater than 15 ppm generally experience difficulty in breathing. Excessive or prolonged exposure causes pulmonary edema and death. The physiological effects of various concentrations of chlorine gas **are** shown in Table 2 along with the limits for chlorine exposure in the workplace. Appendix C includes graphs that estimate the areas affected by various chlorine release scenarios. Exposure to chlorine produces no known cumulative effects.

Table 2. Physiological Responses and Exposure Limits for Chlorine Gas Concentrations

Effects/Emits	Parts per Million (ppm) by Volume
Threshold limit value <sup>(a)</sup>	0.5
Least detectable odor <sup>(b)</sup>	3.5
Least amount required to cause irritation of throat(b)	15
Immediately Dangerous to Life or Health (IDLH) concentration(c)	30
Dangerous for short exposures <sup>(b)</sup>	50
Fatal for brief exposures <sup>(b)</sup>	1,000

<sup>(</sup>a) American Conference of Governmental Industrial Hygienists, 1992.

<sup>(</sup>b) Sax, et al., 1979.

<sup>(</sup>c) National Institute for Occupational safety and Health, 1990.

### **8.0 ANALYSIS METHOD**

The analysis method used in this example process hazard analysis (PrHA) was the hazard and operability (HAZOP) study. The HAZOP study was developed specifically for process industries to identify both safety hazards and operability problems that could compromise a plant's ability to achieve design productivity.

The basic concept behind HAZOP studies is that processes work well when operating under design conditions, and that deviations from process design conditions cause hazards and **lead** to operability problems. In a HAZOP study, guide words are used to assist an analysis team in considering the causes and consequences of deviations from design conditions. The guide words are applied at specific points or "nodes" in a process and are combined with process parameters to identify potential deviations.

The HAZOP study method entails analyzing hazardous events (accidents) to see how they may occur and what undesired consequences are possible. Each sequence of failures and conditions leading to an accident event is a unique scenario. Every accident scenario includes an *initiating event* or cause (e.g., mechanical or human failure), a process deviation(s), an accidental event or consequence, and an impact (injuries and/or damage). Protection may be employed to keep the accident from occurring. Mitigation may reduce the severity of the impact (see Figure 9).

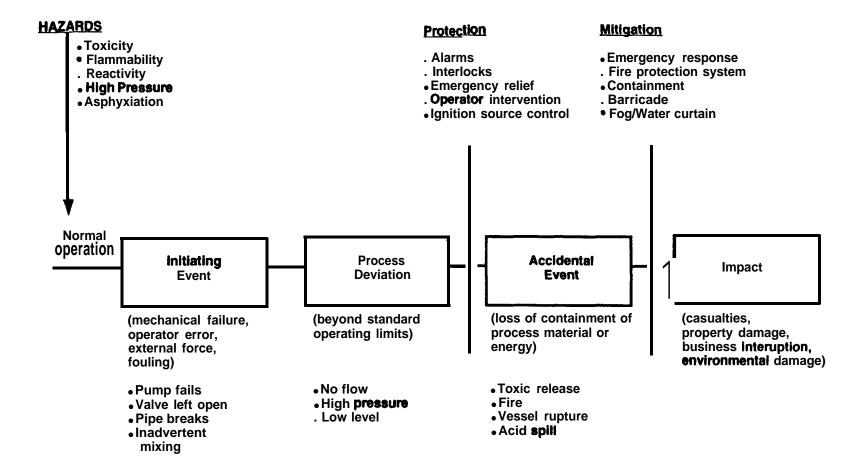
## The HAZOP methodology

- Postulates deviations from design intent
- Examines the causes of the deviations
- Determines the consequences and range of potential impacts if deviations are allowed to continue uncorrected
- Assesses the protection included in the system design to reduce the likelihood of the cause and/or to prevent or minimize the consequences or impacts.

A HAZOP study requires considerable knowledge of the process being studied, its instrumentation, and its operation. This information is usually provided by team members who are experts in these areas. Where weaknesses or safety improvements in the design or operating procedures are identified, the HAZOP study team develops a list of action items to be further addressed.

Based on the level of complexity and the general nature of the chlorination process at the Hanford 300-Area, the HAZOP study is an appropriate PrHA method to analyze the hazards of the operation.

For a more detailed description of the HAZOP study method and other PrHA methods, see the *DOE Guideline: Guide For Chemical Process Hazard Analysis* (*Draft*, **DOE/EH**, March 1993) and the *Guideline for Hazard Evaluation Procedures* (Center for Chemical Process Safety, 1992, 2nd edition).



## 9.0 ANALYSIS TEAM

The hazard and operability (HAZOP) study team consisted of the team leader, Mr. Fred Leverenz, from Battelle's Process Safety and Risk Management Group; Westinghouse Hanford Comparty (WHC) personnel; representatives from the U.S. Department of Energy (DOE) Headquarters and Richland Operations Office; and personnel from the Pacific Northwest Laboratory (PNL) Training Group and Risk and Safety Analysis Group.

Table 3 lists the personnel who participated in the 4-day HAZOP study. Appendix E contains the resumes of the HAZOP study team.

Table 3. HAZOP Study Team Members

PARTICIPANT ORGANIZATION		ROLE
Fred Leverenz	Fred Leverenz Battelle-Columbus	
Karl Agee*	Westinghouse Hanford Company	Team Member
Joe Angyus	Pacific Northwest Laboratory	Team Member
Samuel Camp, Jr.	Westinghouse Hanford Company	Process Operator and Team Member
Rudy Hansen	Pacific Northwest Laboratory	scribe
Sanji Kanth <sup>*</sup>	DOE Headquarters	Team Member
Ken Murphy*	DOE Headquarters	Team Member
Dickie Ortiz	DOE Richland Operations Office	Team Member
Pete Pelto*	Pacific Northwest Laboratory	Team Member
John Piatt*	Pacific Northwest Laboratory	Team Member
Jay Rude	Westinghouse Hanford Company	Process Engineer and Team Member

<sup>\*</sup> Partial attendance

## 10.0 FACILITY SITING ANALYSIS

As part of the process hazard analysis (**PrHA**), a walkdown of the Hanford 300-Area Water Treatment Facility was performed on May 22, 1993. The following is a description of the general layout of the facility.

The Hanford 300-Area Water Treatment Facility is located within the **fences** of the Hanford 300-Area and away from offsite populations. Most **near-by** human activities are related to facility operations and/or chlorine delivery and associated crane manipulations.

The Columbia River is directly east of the Water Treatment Facility. The closest residences are isolated houses on the opposite side of the river, more than **three-quarters** of a mile away. A pump house is located east of the **facility** near the river. The east **access** road, which supports only **low** levels of traffic, is more than 120 feet away, at a lower elevation.

The chlorination room (80 square **feet**) and the chlorine cylinder storage area (300 square **feet**) are on the north side of the 315 Building. The building closest to the chlorination process is the 338 Maintenance Shop. It is more than 60 feet to the west of the chlorination room. This building is being transferred from the Westinghouse Hanford Company **(WHC)** to Kaiser Engineers, Inc., to be used as a **fabrication** shop. About 20 to 40 employees will eventually occupy the building.

Other buildings in the vicinity of the chlorination process are the 337 Office Building (325 employees), which is more than 200 feet to the south, and the 3768 Modular Office Building (15 employees), which is more than 150 feet to the north. To the north of the 3768 Building are the 3769 Modular Office Building (15 employees), the M103 trailer (7 employees), the M105 trailer (9 employees), and the 3770 Modular Office Building (15 employees). All buildings have multiple exits and emergency plans. The emergency plan evacuation route for the 337 Office Building is toward the south, away from the chlorination process. The emergency plan addresses leaks and spills, as well as unusual, irritating, or strong odors.

The regulator for the chlorine cylinders vents near the roof level of the chlorine cylinder storage area. ShutOffs (G 1 and G2) for the chlorine **feed** are inside the storage area. See Appendix C for potential impacts of chlorine releases.

### 11.0 HUMAN FACTORS

The Occupational Safety and Health Administrative (OSHA) rule on process safety management (the PSM Rule) requires the inclusion of human factors in process hazard analyses (PrHAs). Human factors may positively or negatively influence the likelihood of an operator making an error when interacting with a process. For example, if an operator is required to change the position of a valve, but the location of the valve is not specified and/or the valve is not labeled, the operator may have difficulty responding correctly. More positively, if an operator has enough time to complete an action such that he/she can verify the action, then it is more likely that the operator will act correctly.

Human **factors** are included in this hazard and operability **(HAZOP)** study by adding notations in the **CAUSE** or **PROTECTION** column of the HAZOP study worksheets (see Appendix B) immediately after a human error is indicated. The notation used is "—I-IF" for human factors that may negatively influence an operator's performance and "+HF" for human factors that may help an operator to act correctly.

In some places in the HAZOP study worksheets, human interactions/errors are indicated, but no notation is present. If no human **factors** notifications are present, the HAZOP study team judged that the human factors components of that scenario were "normal," expected good practice. For example, the HAZOP study team assumed that **all** equipment **was** labeled.

Table 4 provides a generic checklist for human factors. This list is recommended for use by PrHA teams to help recognize the human factors that influence each accident scenario.

Table 4. Human Factors Checklist

FACTORS	EXPECTED (+)	NEGATIVE (-)
DISPLAYS/CONTROLS	Essy to read/understand	Hard to read/understand/interpret
	Controls accessible	Controls inaccessible
	Display identifies related device	Display does not show device
	Alarms discriminable, relevant	Alarms confusing, irrelevant
	Display mimics action/position	Display is not representational
	Immediate feedback	No immediate feedback
EQUIPMENT	Clearly labeled	Not labeled or mislabeled
	Accessible	Not easily accessed
	Easily operated	Difficult to operate/change position
	Components easy to distinguish	Several components look similar
PROCEDURES	Realistic; reflect the way things are done	Unrealistic; not the way things are done
	Location of devices/action provided	No location of devices/action provided
	Allows unambiguous determination of event in progress	Results in inappropriate diagnosis
	Clear, consistent format	Confused, difficult to read
	Complete and accurate	Missing step in procedure or wrong sequence
COMPETENCE	Operators generally well trained in related procedures	Operators not well trained in related procedures
	Operators have considerable experience	Operators are novices
	Peer review used in certification	No peer review in certification
<b>Operators</b> given periodic feedback on performance		No feedback
	Design changes are appropriately reviewed	Design changes performed without adequate review

Table 4. Human Factors Checklist (Continued)

FACTORS	EXPECTED (+)	NEGATIVE (-)
STRESS	Adequate time available to complete action	Too little time available to complete action
	Shift assignments are permanent, or shift changes do not create time confusion	Shift changes often occur in the middle of the week; double shifts often occur
	Staffing is at an appropriate level	Staff are needed, or some shifts are intentionally short-staffed
	Safety is emphasized	Operators are concerned about 10ss of production if plant inadvertently shut down for safety issue
	Accountabilities are well defined	Accountabilities are poorly defined
	operator performs acceptable number of tasks	Operator must conduct diverse operations within same time period
ENVIRONMENT/ WORKPLACE	Sufficient lighting	Inadequate lighting
	Minimal noise level	High noise level
	Moderate weather	Extreme weather conditions
	Comfortable temperature/humidity	Extreme temperature/humidity
	Low vibration environment	High vibration environment
	Good job aids	No memory support

## 12.0 SUMMARY

During the process hazard analysis (PrHA) of the chlorination process at the Hanford 300-Acre Water Treatment Facility, areas of uncertainty were identified. Twelve action items and recommendations were made by the PrHA team to clarify these uncertainties and to verify process conditions (see Section 4.0). These recommendations are being reviewed to determine whether further action is needed to improve the chlorination system. In addition, procedures were developed during the PrHA exercise to control and avoid potential hazards.

To comply with the Occupational Safety and **Health** Administration **(OSHA)** rule on process safety management (the PSM Rule), all of the PrHA findings and recommendations must be resolved and documented. All actions taken as a result of the PrHA findings must be reported to employees involved in the process and to any other affected individuals. In addition, the PrHA must be reviewed every 5 years to ensure that it is consistent with the current configuration and operation of the chlorination process. The PrHA, related updates, and the documented resolution of the recommendations must be maintained for the life of the process.

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#### APPENDIX A

## PROCEDURES FOR CHANGE-OUT OF CHLORINE CYLINDERS

### APPENDIX A: PROCEDURES FOR CHANGE-OUT OF CHLORINE CYLINDERS

#### **PART I: Removal of Cylinder**

#### Assumptions:

- Replace west cylinder with chlorinator #1 in service (valves G3, G8, G4, S2, W4, G10, Gil, and G12 are closed to supply chlorinator #l).
- Serviceman and operator wear coveralls.
- 1. Notify the 384 Powerhouse and the Hanford Fire Department that the chlorine cylinder change-out is in progress.
- 2. Start the 315B Building vent **fan** and operate it for three (3) minutes before entering. Maintain the vent fan continuously. (Alarms operate at 1 and 5 **ppm.)**
- 3. Enter through the walk-through door.
- 4. Identify the empty cylinder by its weight, and verify the indication of no flow on the cylinder regulator.
- 5. Close the angle (root) valve on the chlorine cylinder.
- 6. Isolate the automatic **switchover** valve. (Close valves G5, G6, and G9.)
- 7. Verify that valves G8 and G4 are closed.
- 8. **Verify** that valve G 1 is open, and open valve G3. Wait two (2) minutes and verify that there is no flow at the chlorinator in service. Verify that the high-vacuum alarm is actuated.
- 9. Close valves G 1 and G3. Open valves G6 and G9, and verify that the high-vacuum alarm clears.
- 10. Chlorine serviceman dons the **facemask**, and operator dons self-contained breathing apparatus **(SCBA)**. Then they verify the operation of the personal protective equipment.
- 11. Slowly disconnect the regulator, check it for **leaks**, and set it on the floor.

- 12. **Install** the cap on the cylinder angle valve, and install the protective hood.
- 13. Position the crane and cylinder truck for loading; open the roll-up door; remove the chocks; and push the cylinder out to the stops.
- 14. Release the chain binders, and turn the cylinder over to the hoist and rigging crew.
- 15. Install the spreader bar, lift the cylinder, and place it on the flatbed truck.
- 16. Secure the cylinder and transport it.
- 17. Close the roll-up door, and exit through the walk-through door.

#### **PART II: Installation of Replacement Cylinder**

- 1. Turn on or verify that the storage room exhaust fan is on.
- 2. Position the crane for unloading.
- 3. Position the chlorine transport truck for unloading.
- 4. Verify that the chlorine cylinder trolley is in position to receive the cylinder.
- 5. Release the cylinder binder(s) on the transport vehicle.
- 6. Install the lifting bar, and lift the cylinder.
- 7. Place the cylinder on the trolley.
- 8. Remove the lifting bar, removing it from the immediate area.
- 9. Secure the cylinder to the trolley with chain binders (2).
- 10. Enter through the walk-through door, and open the roll-up door.
- 11. Push the trolley and the chlorine cylinder into the building and against the rail stop. Install the wheel chocks.
- 12. Request the chlorine serviceman to remove the protective hood from the chlorine cylinder.
- 13. Observe the position of the cylinder angle valves. If the valves are not in vertical alignment, **loosen** the chain binders and rotate the cylinder to obtain vertical alignment of the valves, and then tighten the chain binders.
- 14. Chlorine serviceman dons the facemask respirator, and operator dons self-contained **breathing** apparatus **(SCBA)** equipment. Then they verify the operation of the personal protective equipment.
- 15. Verify that the chlorine cylinder gas angle valve is closed.
- 16. Check for leaks while slowly removing the protective cap from the cylinder gas angle valve.
- 17. Clean the sealing surface of the gas angle valve and the vacuum regulator. Visually inspect the regulator valve body for damage.

- 18. Install a new lead **seal**. Attach the regulator to the cylinder gas valve, and secure it in place by tightening the yoke assembly.
- 19. Check for leaks. Slowly open the chlorine cylinder gas supply valve.
- 20. Adjust the cylinder weight **scale** to indicate 2,000 pounds of product available in the cylinder.
- 21. Open system supply valves **G1** and **G5**.
- 22. Record in the log book the chlorine cylinder identification number and the **scale** weight.
- 23. Report any deficiencies to the supervisor for initiation of **necessary** corrective action.
- 24. Notify the Hanford Fire Department and the 384 Powerhouse that the chlorine cylinder change-out activities are complete.
- 25. Close the roll-up door, and exit through the walk-through door.

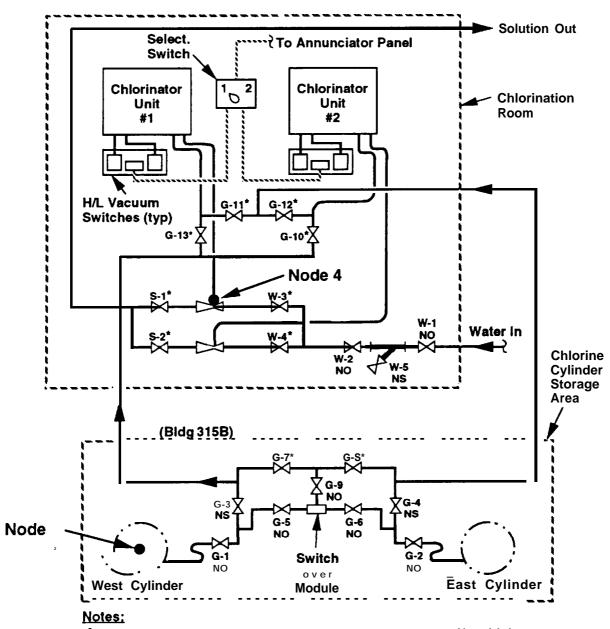
# APPENDIX B HAZOP STUDY WORKSHEETS

#### APPENDIX B: HAZOP STUDY WORKSHEETS

Two independent chlorination systems are installed at the Hanford 300-Area Water Treatment Facility. These systems can be operated separately or in parallel. Because they are normally operated separately, this HAZOP study assumes only chlorination system #1 is operating, and that valves G-12, G-1 1, G-10, G-8, G-4, G-3, S-2, and W-4 are closed.

The following worksheets document the HAZOP study. The chlorination process was separated into four study nodes. These four nodes are shown on Figure B-1 (Nodes 2 and 4) and Figure B-2 (Nodes 1, 3, and 4). Nodes 5 and 6 cover the procedures for change-out of chlorine cylinders (see Appendix A).

The HAZOP worksheets for the six nodes use HAZOP guide words to determine possible deviations from process design conditions. Causes are **described**, including positive and negative human factors influences ("+HF" for positive influences and "-HF" for negative influences). Consequences of accident scenarios are estimated qualitatively for each process deviation. Protection and mitigating **factors** are described, including positive and negative human factors influences. The action/comment column includes both action items and justifications for no further action.



- Position depends on which chlorinator or cylinder and/or chloine supply line is in-service
- NO Normally open
- NS Normally shut

**39306007.** 1A

Figure RI. Chlorination Process, Study Nodes 2 and 4

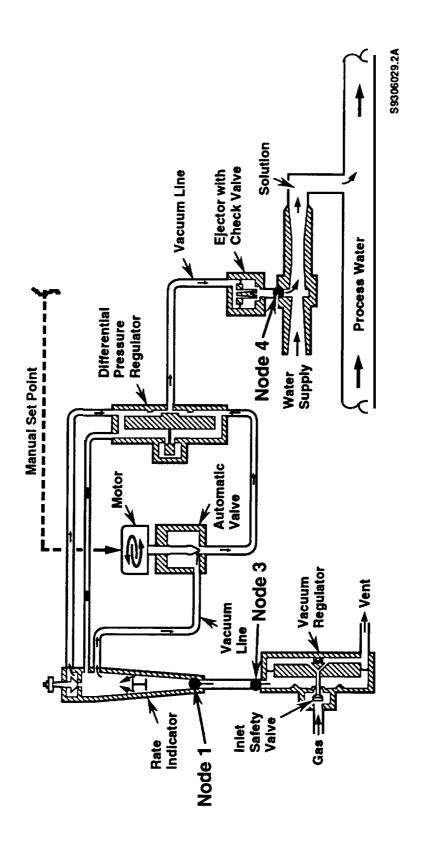


Figure B-2. Chlorination Process, Study Nodes 1, 3, and 4

MACON PACINIC	onec i					PAGE B-3
'LANT/OPER/ .INE/VESSEL/		reatment Facility / Chlorination	Process	REVIEW DATE: 5/1 8/93 DRAWING NO.: Automatic Gas	Feed Sy	rstem (Figure B-2)
DESIGN INTENTION Transfer C1 <sub>2</sub> Vapor to Rotameter 20-60 lbs/day at 26-inch mercury vacuum at 65°F through ambient			REVIEW TEAM: K. Agee, J. Rude, S. Camp, F. Leverenz, K. Murphy, S. Kanth, D. Ortiz, J. Angyus, P. Pelto, J. Piatt, R. Hansen			
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES	PROTECTION	SCE- NARIO	ACTION / COMMENTS
No	No Flow	Valve closed (G-1, G-5, G-7, G-9, and G-1 3).  Failed closed.  Inadvertently closed,  I-HF: valves located dose to each other   +HF:flow directions indicated by valve position; valve handles different.]  Poly line crimped by activity (e.g., maintenance) in area.  Screen blocked in regulator on cylinder.	Decreased Cl <sub>2</sub> residual in water, violates state code (WAC 246-290). (Takes 1-2 hours to occur.)  If continued undetected, a bacterial problem could result with illness across the site (within a day).	1) Automatic switch-over if the valves G-1 and G-5 are closed. 2) High vacuum alarm; the operator diagnoses and restores the system if possible.  [-HF:many potential causes for this dorn; no procedures for diagnosis   + HF: time for diagnosis is long; rotameter flow indication aids diagnosis.] 3) Low C1_residual during surveillance. a) The filter plant is checked every 2 hrs. b) The tour operator checks around the grid (at 12 points/shift).  [-HF: operator normally adjusts C1_2 flow via controller, could try to adjust for low C1_2 without noticing rotameter is at no flow   + HF: several checks by different operators before consequence occurs.]  Mitigation: Restrict usage of potable water when low C1_2 is detected,	1-1	Sufficient protection.
More	More flow	No causes in this segment.			1-2	
Less	Less flow	Valves partially closed (same valves as #1-1).	Same as #1-1 (no flow), except it would take longer.	Same as Protection in #1 -1, 1) and 2) (if vacuum from restricted flow is high enough), and 3).	1-3	Protection sufficient.

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'LANT /OPER .INE/VESSEL		reatment Facility / Chlorination	Process	REVIEW DATE: 5/1 8193 DRAWING NO.: Automatic Gas	Feed Sy	rstem (Figure B-2)	
)ESIGN INTE	NTION: Transfer at 26-ind	r Cl <sub>2</sub> Vapor to Rotameter 20-6 ch mercury vacuum at 65°F th	0 lbs/day rough ambient	REVIEW TEAM: K. Agee, J. Rude, S. Camp, F. Leverenz, K. Murphy, S. Kanth, D. Ortiz, J. Angyus, P. Pelto, J. Piatt, R. Hansen			
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES	PROTECTION	SCE- NARIO	ACTION / COMMENTS	
Reverse	Reverse flow	Valve S-1 closed. Failed closed. Inadvertently closed, —HF: valves located close to eech other   + HF: flow direction indicated by valve position; valve handles different.]	Water enters the chlorine vapor system with damage to equipment and seals and there is potential for leaks later if it is not repaired:  • "In" leakage of air when operating ejector  • Small "out" leakage of Cl <sub>2</sub> when vacuum from ejector is interrupted; minor irritation if staff present.	1) Check valve at ejector. 2) Low vacuum alarm. [-HF: mew potential causes for this alarm; no procedure for diagnosis]. 3) Same protection as #I-1, 3).	1-4	Check on possibility of backflow past rotameter and respond accordingly by modifying administrative procedures.	
Vore	High Temperature	No causes in this segment.			1-5		
_ess	Low temperature	No causes for temperature low enough to cause a problem.			1-6		
More	High pressure	No causes in this segment.			1-7		
_ess	Low pressure	No causes in this segment.			1-8		
As well	Air into C1 <sub>2</sub>	Leak in polyethylene tubing/pipe, valve stem, etc, (Replacement of tubing every two years reduces the likelihood of failure.)  Potential for dissimilar material to thermally expand or contract from temperature extremes.	Low Cl <sub>2</sub> for water treatment.  If continued undetected, a bacterial problem could result with illness across the site.	Check of Cl <sub>2</sub> residuals during surveillance may detect.  a) The filter plant is checked every 2 hrs. b) The tour operator checks around the grid (at 12 points/shift).   -HF: operator normally adjusts Cl <sub>2</sub> flow via controller, could try to adjust for low Cl <sub>2</sub> without noticing rotameter is et no flew  +HF: several checks by different operators before consequence occurs.] Mitigation: Restrict usage of potable water when low Cl <sub>2</sub> is detected.	1-9	Consider adding procedures that verify the vacuum holds after system shutdown (to be use when tubing is replaced and chlorinators are changed each month).	

						11702511	
LANT/OPERA		eatment Facility / Chlorination	n Process	REVIEW DATE 5/1 8/93  DRAWING NO.: Automatic Gas Feed System (Figure B-2)			
resign Intention: Transfer Cl <sub>2</sub> Vapor to Rotameter 20-60 lbs/day at 26-inch mercury vacuum at 65°F through ambient			REVIEW TEAM:  K. Agee, J. Rude, S. Camp, F. Leverenz, K. Murphy, S. Kanth, D. Ortiz, J. Angyus, P. Pelto, J, Piatt, R. Hansen				
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES	PROTECTION	SCE- NARIO	ACTION / COMMENTS	
\s well is (cont.)	Air into Cl <sub>2</sub>	Leak in polyethylene tubing/pipe, valve stem, etc. (Replacement of tubing every two years reduces the likelihood of failure. )  Potential for dissimilar material to thermally expand or contract from temperature extremes.	Potential for damage to seals/corrosion from HCl forming due to moisture in air,  Same as #1-4,	Operator to check rotameter every 2 hrs. Can visually detect air, if familiar with its appearance.  Vacuum gage on chlorinator may show decrease in vacuum.  I—HF: these require operator with enough experience to recognize ornewhat subtle indications; "novice" not likely to detect. I	1-10	Minor consequences.	
		Leak in system after replacement of tubing.  I—HF:no procedure written for replacement of tubing, or *y*tem integrity verification after replacement.]	Same as #I-9 and #I-IO.	Same as #I-9 and #1-10.	1-11	Same as #I-9 and #1-10.	
Part of	No meaningful deviations						

#### AZOP HYCHRUSHEET

PLANT/OPERATION: Water Treatment Facility / Chlorination Process  Node 1  PESIGN INTENTION: Transfer Cl <sub>2</sub> Vapor to Rotameter 20-60 lbs/day at 26-inch mercury vacuum at 65°F through ambient				REVIEW DATE 5/1 8193  DRAWING NO.: Automatic Gas Feed System (Figure B-2)  REVIEW TEAM: K. Agee, J. Rude, S. Camp, F.Leverenz, K. Murphy, S. Kanth, D.Ortiz, J. Angyus,			
GUIDE DEVIATION CAUSE CONSEQUENCES			P, Pelto, J. Piat				
Other :han	Air into ejector	Line break (either poly break or schedule-80 steel break inside or outside of building). Maintenance activity could be the cause of failure, especially poly.	Loss of C <sub>2</sub> to water treatment see #1-1 ).	1) Low vacuum alarm, may have Cl <sub>2</sub> alarm; the operator diagnoses and switches to alternate supply.  [-HF: many potential causes for this alarm; no procedures for diagnosis.  2) Cl residual checks (See #7-1, Protection 3).	1-12	Low likelihood.	
			Cl <sub>2</sub> release (up to 3/8-inch release). Potential for injuries and fatalities near 315 Building and neighboring buildings.	Regulator shuts off on loss of vacuum.  Mitigation: Cl <sub>2</sub> alarm (local and remote). Site-wide emergency response (alarm designed for leaks inside building). "Chlorinator trouble alarm" (31 5 common alarm) with tour operator response.	1-13	Low likelihood. Cause and sufficient protection.  Verify that the adjacent buildings have received information on chlorine in their HAZCOM program.	

Hazard and Operability Study Worksheet

FOR * 171-111							
LANT/OPER	ATION: Water Ti	reatment Facility / Chlorinatio	n Process	REVIEW DATE:	5/1 9193	_	
Node 2  ► Storage cylinder provides → gas to regulator at 6 approximately 75 psig to 150 psig (at 110 "F); 20-		regulator at 65°F to ambient, t 110"F); 20-60 lbs CIZ/day.	DRAWING NO.: REVIEW TEAM:	Chlorination Process Flow Diagram (Figure B. F. Leverenz, S. Camp, J. Rude, K. Agee, S. Kanth, K. Murphy, D. Ortiz, J. Angyus, R. Hansen			
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES	PROTECTION		SCE- NARIO	ACTIONS/COMMENTS
10	No Cl <sub>2</sub> provided	Tank is empty.	Same as #I-1.	Same as #1-1 and weight check.		2-1	Same as #I-1.
1		Tank valve is closed.	Same as #I-1.	Same as #I-1.		2-2	Same as #I-I.
		Internal tank tubes are plugged/defective (blocked).	Same as #I-1.	Same as #I-1.		2-3	Same as #I-1.
Vore	More Cl <sub>2</sub> provide d	No causes.					
_ess	Less Cl <sub>2</sub> provided	Valve partially closed [-HF:valvedoes not readily indicate amount open.] Internal tank tubes partially plugged.	Same as #2-2 and 2-3 except takes longer to	Same as #2-2 and 2-3.		2-4	Same as #2-2 and 2-3.
More	High temperature	Heater fails "on" during summer heat.	If the temperature is greater than 160° F, the fusible link may release resulting in a Cl <sub>2</sub> release. Potential for injuries and fatalities near the 315 Building and neighboring buildings.			2-5	Calculate temperature based on heat input versus heat loss for this scenario. Base further recommendation items on the results,

PLANT/OPER	RATION Water T	reatment Facility / Chlorination	on Process	<b>REVIEW</b> DATE: 5/1 9193			
	Node 2  DESIGN INTENTION: Storage cylinder provides GJ gas to regulator at 65°F to ambient, approximately 75 psig to 150 psig (at 11 O"F); 20-60 lbs Cl <sub>2</sub> /day.			DRAWNG NO.: Chlorination Process Flow Diagram (Figure B-1) REVIEW TEAM: F. Leverenz, S, Camp, J. Rude, K. Agee, S. Kanth, K. Murphy, D. Ortiz, J. Angyus, R. Hansen			
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES	PROTECTION	SCE- NARIO	ACTIONS / COMMENTS	
More [cont.)		Fire  The following reduces the likelihood of a fire:  Internal fire: no combustible or flammable materials are stored in the building,  External fire: there are no likely fire sources.  Housekeeping procedures are used to prevent combustible or flammable materials from entering the building.	If fusible plug(s) work, release will occur via plug, If not, a BLEVE could result, Same as #2-5.	None.	2-6	Fire is very unlikely.	
Less	Low temperature	Heater fails in the winter/cold weather,	Potential reduction in C1, feed rate; no significant consequence,		2-7	Minor consequences.	
More	High Pressure	Cylinder is received overfilled.	Unknown	Check cylinder weight against the weight of a properly filled chlorine cylinder.  [-HF: procedure requires operator to 'zero' weight for new cylinder; may not notice overweight.]	2-8	Check pressure potential from chlorine cylinder and the system (regulator) response. Determine whether the fusible plug will open with high pressure.	
_ess	Low pressure	Covered under low temperature (#2-7); no additional causes related to hazards.			2-9		
As well	Other material added	C1₂contaminated.	Unknown		2-10	Check with vendor regarding possible contamination material for scenarios 2-10 and 2-11. Take appropriate recommendation/action.	

PAGE B-1 5

PLANT / OPER	LANT / OPERATION: Water Treatment Facility / Chlorination Process				5/1 9193		
			DRAWING NO.: Chlorination Process Flow Diagram (Figure B-1) REVIEW TEAM: F. Leverenz, S. Camp, J. Rude, K. Agee, S. Kanth, K. Murphy, D. Ortiz, J. Angyus, R, Hansen			J. Rude, K. Agee,	
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES	PROTECTION		SCE- NARIO	ACTIONS/COMMENTS
Other than	Another material loaded	Cylinder contains something other than chlorine (e. g., sulfur dioxide uses same size container),	Unknown			2-11	See above.
Part of	No meaningful deviations	,					

Hazard and Operability Study Worksheet

HAZOP-WORKSHEET

LANT/OPER	ATION: Water Ti	reatment Facility/Chlorinatio	n Process	REVIEW DATE: 5/1 9193		
	Node 3  Provide Clyfrom storage cylinder to vacuum line at 25 inches of Hg at 65°F to ambient with 20-60 lb./day.		PRAWING NO.: Automatic Gas Feed System (Figure B-2)  REVIEW TEAM: F. Leverenz, S. Camp, J. Rude, K. Agee, S. Kanth, K. Murphy, D. Ortiz, Joe Angyus, R. Hansen			
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES	PROTECTION	SCE- NARIO	ACTIONS / COMMENTS
70	No flow	Broken diaphragm, stuck open relief valve, or leak in vacuum side of regulator occurs.	Loss of Cl <sub>2</sub> flow (same as #1-12).	Same as #1-9.	3-1	Consider #1 -9 recommendation; would need to close the C1, cylinder block valve.
<b>Viore</b>	More flow	Regulator fails open.	Release of Cl <sub>2</sub> through the relief valve and vent (same as #1-13). Potential for injuries/fatalities near the 315 Building and neighboring buildings.	None.  Mitigation: Cl <sub>2</sub> alarm (local and remote). Site-wide emergency response (alarm designed for leaks inside building). "Chlorinator trouble alarm" (31 5 common alarm) with tour operator response.	3-2	The cause seems to have a low likelihood. The vendor should be contacted to determine the failure experience (corrosion, water, etc.). If cause seems more likely after investigation, controls such as remote shutoff at C½ cylinder (and power ted-safe] should be considered.
_ess	Low flow	Regulator doesn't open far enough.	Same as #2-4,	Same as #2-4 .	3-3	Same as #2-4.
Reverse	Reverse flow	No causes in this segment.			3-4	
More	High temperature	No causes this segment,			3-5	
_ess	Low temperature	No causes this segment.			3-6	
More	High pressure	No additional causes (see 3-2).			3-7	
Low	Low pressure	No additional causes (see 3-3).			3-8	
Part of	No meaningful deviation this segment				3-9	

HAZOP, WORKSHEET

LINE/VESSEL/	PLANT/OPERATION: Water Treatment Facility / Chlorination Process LINE/VESSEL/NODE: Node 3  DESIGN INTENTION Provide Ciferom storage cylinder to vacuum line at 25 inches of Hg at 65°F to ambient with 20-60 lb./day.  PROVIDED STATEMENT OF THE ST				J. Rude, K. Agee,			
GUIDE WORD	DEVIA	TION	CAUSE	CONSEQUENCES	PROTECTION		SCE- NARIO	ACTIONS /COMMENTS
As well as	Material atmosph side of t regulator	eric he	Sand, water, bugs, dust, etc.	Blocked vent line; if an over-pressure event occurs (3-2) the vacuum line could become over-pressured; the vacuum line may not hold under pressure (same as #1-13).	Vent screen will protect somewhat (same as xI-13).		3-10	Verify that the screen is in place.

Hazard and Operability Study Worksheet

PLANT/OPERA	TION: Water Tr	eatment Facility / Chlorinatio	n Process	REVIEW DATE:	5/1 9/93		
LINE/VESSEL/	NODE: Node 4	·		<b>DRAWING NO.:</b> Automatic Gas Feed System and Chlorination Process Flow Diagram (Figures B-1 and B-2)			ystem and Chlorination (Figures B-1 and B-2)
DESIGN INTENTION: Provid 15 to ejector at 25 inches of 20-60 lb/day, 65°F to ambient			Hg, vacuum,	F. Leverenz, S. Camp, J. Rude, S. Kanth, K. Murphy, D. Ortiz, J. R. Hansen			, J. Rude, K. Agee, D. Ortiz, Joe Angyus,
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES	PROTE	CTION	SCE- NARIO	ACTIONS/COMMENTS
No	No flow	Motor-controlled rate valve closed.  Failed closed.  Operator closes rate control valve inadvertently.  He: up/down* key pad with digital readout display of position.]  Ejector check valve failed closed.  Valves plugged by dirt.	Same as #I-1.	Same as #I-1.		4-1	Protection sufficient,
More	More flow	Rotameter opened too far. Rate valve opened too far.	Objectionable tastes/vapors in the water.	flow on ro tank.  I - HF: operate digital is not life rotameter flow 2) Surveillance "residuals"	e of	4-2	Minor consequence.

AZUFWURKSHEET PAGE B-20

PLANT /OPER	ATION: Water T	reatment Facility / Chlorination	n Process	REVIEW DATE	5/19193		
.INE/VESSEL/	NODE: Node 4	DRAWING NO.: Automatic Gas Feed System and Chlorination Process Flow Diagram (Figures B-1 and B-2)					
DESIGN INTENTION: Provid∿ੀ to ejector at 25 inches of Hg, va 20-60 lb/day, 65°F to ambient			Hg, vacuum,	REVIEW TEAM:	J. Rude, K. Agee, D. Ortiz, Joe Angyus,		
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES			SCE- NARIO	ACTIONS /COMMENTS
_ess	Less flow	Plugged ejector.  Rota meter closed too much,  Rate valve not opened enough.  [-HF: possible error m residual sample or calculation   +HF: "up/down" key pad with digital readout display of position].  Operator does not reset to a higher value when the demand increases.  [-HF: operators depend on memory to complete actions.]  PLC controller fails.	Same as #1-3.	Same as #I -3.		4-3	Sufficient protection.
More/less	High or low pressure	Differential pressure regulator.	Unknown			4-4	How the differential pressure regulator operates is unknown. The valve's operation should be checked and the potential for a pressure deviation should be assessed.

HAZOP.WORKSHEET

LANT/OPER	ATION: Water Tr	eatment Facility / Chlorinatio	n Process	REVIEW DATE	5/1 9/93		
INE/VESSEL/	NODE: Node 4			DRAWN(3 NO.:			ystem and Chlorination (Figures B-1 and B-2)
PESIGN INTE	NTION: Provida 20-60 lb	ស្ទ to ejector at 25 inches of /day, 65°F to ambient	Hg, vacuum,	REVIEW TEAM: F. Leverenz, S. Camp, J. Rude, K. Agee, S. Kanth, K. Murphy, D. Ortiz, Joe Angyu R. Hansen			
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES	PROTEC	CTION	SCE- NARIO	ACTIONS/COMMENTS
<b>Nore</b>	High temperature	Chlorinator heater fails "on" in summer,	Possible water pipe rupture if the temperature exceeds the PVC's strength, Small chlorine release (no health effects expected),	None.		4-5	Minor consequences.
			PLC operational limits. The PLC could malfunction if temperature is too high (see less/more flow scenario, #I-2 and #I-3).	Same as #I-2 a	Same as #I-2 and #1 -3.		(PLC operating range: 14° F-122° F,)  Protection sufficient (#1 -3) and minor consequences (#1 -2).
.ess	Low temperature	Heater fails during cold weather [winter).	Out-of-service water pipe breaks (water freezes in the line).	The operator's of the facility.	not <b>note</b> while it is still tor will likely note	4-7	Minor consequences.
			Safety shower and eye wash freezes. There is potential for more serious injury if an incident occurs during unavailability.	Safety shower wash lines are		4-8	Low likelihood that an incident occurs the same time freezing occurs.
<sup>2</sup> art of	No meaningful deviation						
As well 3s	Air into chlorine vacuum line	Leak in the line/fittings: potential for dissimilar material to thermally expand or contract from temperature extremes.	Same as #I-9 and #1-10.	Operator check residuals, (Sam Protection 3 of	ne as	4-9	Same as #I-9 and #1-10.
Reverse	Heverse Tiow	Already coverea #1-4.				4-10	Same as #1-4.

#### AZOP WURKSYEET

PLANT/OPERATION: Water Treatment Facility / Chlorination Process REVIEW DATE:				REVIEW DATE:	REVIEW DATE: 5/1 9/93			
LINE/VESSEL/	NODE: Node 4			DRAWING NO.: Automatic Gas Feed System and Chlorination Process Flow Diagram (Figures B-1 and B-2)				
pesign intention: Provides to ejector at 25 inches of Hg, vacuum, 20-60 lb/day, 65°F to ambient			f Hg, vacuum,	REVIEW TEAM: F. Leverenz, S. Camp, J. Rude, K. Agee, S. Kanth, K. Murphy, D. Ortiz, Joe Angyus R. Hansen				
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES	PROT	ECTION	SCE- NARIO	ACTIONS / COMMENTS	
Other than	Air only into injector	Line break in vacuum line.	Same as \$1-12.	Same as #1-1	2.	4-11	Same as #1-12.	
None	No level	Chlorine tank failure (e.g., structural flaw).	Release of contents. Potential for injury and fatalities of staff in the surrounding area.	None,  Mitigation: Cl <sub>2</sub> alarm (local and remote). Site-wide emergency response (alarm designed for leaks inside building), "Chlorinator trouble alarm" (31 5 common alarm) with tour operator response.		4-12	Low likelihood.	
No	Loss of utility (off-site power)	Loss of electric power; water pumps discontinue operating. (Loss of vacuum to chlorinator).	Cl <sub>2</sub> is release through the vent, Cl <sub>2</sub> contacts back flow preventers with potential damage to equipment. Up to 3/8-inch leak with potential for injuries and fatalities near 315 Building and neighboring buildings.	Regulator safe Mitigation: (Sa #4-12).		4-13	Note: the detector has battery backup and an alarm on standby power,  Verify that the monthly PM includes checking the backup battery for the chlorine alarm.  Note: there are plans to put water pumps on standby power, which will make this "cause" less likely,	

lazard and Operability Study Worksheet

HAZOP-WORKSHEET

LANT/OPER	RATION: Water Tr	eatment Facility / Procedures		REVIEW DATE	5/20193		
ine/vessel	./NODE: Node 5			DRAWING NO.:	Procedures for Cylinders (see		nge-out of Chlorine x A)
ESIGN INTE		g Empty Chlorine Cylinder (wingful deviations have been o	,	F. Leverenz, S. Camp, J. Rude, K. Age S. Kanth, K. Murphy, D. Ortiz, J. Ang J. Piatt, R. Hansen			
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES	PROT	ECTION	SCE- NARIO	ACTIONS/COMMENT
	(1) Notify the 3	84 Powerhouse and the Hanfo	ord Fire Department that the c	hlorine cylind	er change-out is	in progi	ess.
10	Skip step	Supervisor does not notify.	May increase response time/readiness of personnel because of no advanced warning. False response upon disconnect of regulator resulting in C1, alarm (Step 1 1)0	None,		5-1	Minor consequences.
	(2) Start the 3 1	I5B Building vent fan and ope	erate it for 3 minutes before e	ntering. Main	tain the vent far	continu	ously.
No/less	Skip step. (Operate less than 3 min.)	The C1 <sub>2</sub> plant operator does not start the fan,	Possible exposure if a leak exists and the detector failed,  Possible irritation with low likelihood of injury.		function alarm or that detector ay proceed and present.	5-2	Low likelihood.
	(3) Enter throu	gh the walk-through door.	,	•			,
	No meaningful deviation					5-3	

Meter T				E/20/02						
	reatment Facility / Procedures		Ī		, 4ha Ob	man out of Chlarina				
			DRAWING NO.:	Cylinders (see	Appendi	x A)				
ITION: Removir	ng Empty Chlorine Cylinder (w	est cylinder)	REVIEW TEAM: F. Leverenz, S. Camp, J. Rude, K. Agee, S. Kanth, K. Murphy, D. Ortiz, J. Angyus, J. Piatt, R. Hansen							
ds without mear	ningful deviations have been o	mitted from this table.								
DEVIATION	CAUSE	CONSEQUENCES	PROT	ECTION	SCE- NARIO	ACTIONS/COMMENTS				
(4) Identify the empty cylinder by its weight, and verify the indication of no flow on the cylinder regulator.										
Skip step	Cl <sub>2</sub> plant operator does not heck cylinder weight and or indication of no flow.	f the wrong cylinder is selected, there is loss of C1 <sub>2</sub> o the chlorinator (same as #1-1).	received vacuum.  {-HF: may a normal alarm cylinder.}  2) Hoisting crew not is heavie (+HF: crew change-out data telear. {-HF: 'rev	on loss of  mesume this is e in for change-out of  and rigging ices that tank in than normal. is experienced in of cylinder.}  alarm does erse indication is	5-4	diner consequences.				
		Release of contents of full cylinder at Step 11.  njury/potential fatality of the plant operator.  Injury/fatality potential in nearby buildings.	is closed.  2) At Step 8 chlorinat checked. alarm has checked. 3) At Step operator leaks wh regulator [-HF: this e judgement of detect that  Mitigation: p protective ed  Mitigation: o HAZMAT tea	B the or flow is Actuated s been  11 plant checks for en removing  tep requires on how to remove to tank is still open.)  personal quipment.  beserver radios am; emergency	5-5	Protection sufficient.				
	NODE: Node 5  TION: Removir  ds without mean  DEVIATION  (4) Identify the	TION: Removing Empty Chlorine Cylinder (weds without meaningful deviations have been of DEVIATION CAUSE  (4) Identify the empty cylinder by its weight,  Skip step 312 plant operator does not sheck cylinder weight and	Removing Empty Chlorine Cylinder (west cylinder)  ds without meaningful deviations have been omitted from this table.  DEVIATION  CAUSE  CONSEQUENCES  (4) Identify the empty cylinder by its weight, and verify the indication of no skip step  Cl <sub>2</sub> plant operator does not sheck cylinder weight and or indication of no flow.  f the wrong cylinder is selected, there is loss of C1, o the chlorinator (same as f1-1).  Release of contents of full cylinder at Step 11.	REVIEW TEAM:  Removing Empty Chlorine Cylinder (west cylinder)  REVIEW TEAM:  DEVIATION  CAUSE  CONSEQUENCES  PROT  (4) Identify the empty cylinder by its weight, and verify the indication of no flow on the sheck cylinder weight and or indication of no flow.    1, plant operator does not sheck cylinder weight and or indication of no flow.    5 the wrong cylinder is ielected, there is loss of C1, or the chlorinator (same as f1-1).    1 At Step Fince weighted in the cylinder is ielected, there is loss of C1, or the chlorinator (same as f1-1).    1 At Step Fince weighted in the chlorinator (same as f1-1).    2	Removing Empty Chlorine Cylinder (west cylinder)  Review Team: F. Leverenz, S. S. Kanth, K. N. J. Platt, R. Har  DEVIATION  CAUSE  CONSEQUENCES  PROTECTION  (4) Identify the empty cylinder by its weight, and verify the indication of no flow on the cylinder regulate indication of no flow on the cylinder regulater indication of no flow on the cylinder indication of no flow on the cylinder regulater indication of no flow on the cylinder indication of no flow	DRAWING NO.:   Procedures for the Charge   Procedures   Pr				

14.AZOR JWORKSHEFT PAGE B-25

14 <b>.6309 JVOR</b> K	**************************************					PAGE B-25		
'LANT/OPERA .INE/VESSEL/I		reatment Facility / Procedures		REVIEW DATE: 5/20/93 DRAWING NO.: Procedures for Cylinders (see		nge-out of Chlorine x A)		
)ESIGN INTER	NTION: Removir	ng Empty Chlorine Cylinder (w	est cylinder)	REVIEW TEAM: F. Leverenz, S. Camp, J. Rude, K. Agee, S. Kanth, K. Murphy, D. Ortiz, J. Angyus,				
<b>Buide Wor</b>	ds without mean	ningful deviations have been o	mitted from this table.	J. Piatt, R. Hansen				
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES	PROTECTION	SCE- NARIO	ACTIONS /COMMENTS		
	(5) Close the a	ngle (root) valve on the chlori	ne cylinder.					
No	Skip step	Cl <sub>2</sub> plant operator does not close the valve.	Release of the remaining cylinder contents at Step 11.  Injury to plant operator.  Injury to staff in nearby buildings.	Step 8 chlorinator flow checked/alarm actuated.     Step 11 slowly disconnect regulator and check for leaks.  Mitigation: personnel protective equipment.  Mitigation: observer radios hazmat team; emergency response initiated.	5-6	Sufficient protection.		
Less	Valve partially closed.	Plant operator does not close the valve completely. [-HF:valve provides no indication of position.]	Lesser consequence than #5-6. Injury to plant operator.	At Step 11 check for leaks at disconnect.  [-HF:• MW as #5-5, 3).]  Mitigation: Personal protection equipment.	5-7	Sufficient protection.		
Reverse	Valve opened all the way	Plant operator opens rather than closes the valve.  [ -HF: valve provides no indication of position, and full open 'feels' like full closed.]	Same as #5-6.	Same as #5-6.	5-8	Sufficient protection.		
	(6) Isolate the	automatic switch-over valve.	(Close valves G5, G6, and G	9).				
No	Skip step	Plant operator skips step.	At Step 11 when disconnect slightly larger release of Cl <sub>2</sub> .  Minor irritation.	At Step 8, flow/vacuum alarm check.	5-9	Sufficient protection.		

AZOP WORKSHEET PAGE B-26

LANT/OPE		eatment Facility / Procedures	3	REVIEW DATE:	5120/93		
.INE/VESSEL	./NODE: Node 5			DRAWING NO.: Procedures for the Change-out of Chlorine Cylinders (see Appendix A)			x A)
DESIGN INT		g Empty Chlorine Cylinder (w	• •	REVIEW TEAM: F. Leverenz, S. Camp, J. Rude, K. Age S. Kanth, K. Murphy, D. Ortiz, J. Angy J. Piatt, R. Hansen			J. Rude, K. Agee, D. Ortiz, J. Angyus,
Juide Wo	ords without mean	ingful deviations have been o	omitted from this table.		J. Flatt, R. Ha	7	
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES	PROT	ECTION	SCE- NARIO	ACTIONS/COMMENTS
	(7) Verify that v	valves <b>G8</b> and G4 are closed					
No	Skip step	Plant operator skips this step.	No consequences.			5-1o	No consequences.
No	Skips step	Plant operator skips this step.	Same as #5-9.	1 ) Slow disconnect and leak check at Step 11. [-HF:see #5-5, 3).]		5-11	Sufficient protection.
				protective eq	uipment.		
_ess	Less time	Plant operator proceeds without waiting 2 min.	Lesser consequence than #5-n,	1) Flow check at chlorinator. 2) High vacuum alarm at Step 11, 3) Slow disconnect and leak check at Step 11. [-HF:see #5-5, 3}.]		5-12	Sufficient protection.
				Mitigation: perotective equ			
Part of	Skips check on step	Plant operator skips "checks" of vacuum alarm and flow.	Loss of protection for this step and for previous steps,	None.		5-13	No direct consequence.
	Skips opening G3	Plant operator does not open G3.	Same as #5-11.	Same as #5-	12.	5-14	Sufficient protection.

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- THE OF WORK	CONTECT						PAGE D
'IANT/OPER	ATION: Water Ti	reatment Facility / Procedure	es	REVIEW DATE:	5/20/93		
NE/VE88EL	/NODE: Node 5			DRAWING NO.: Procedures for the Change-out of Chlorin Cylinders (see Appendix A)			
esign inte Suide Wo		ng Empty Chlorine Cylinder ( ningful deviations have been	REVIEW TEAM: F, Leverenz, S. Camp, J. Rude, K. Agee, S. Kanth, K. Murphy, D. Ortiz, J. Angyus, J. Piatt, R. Hansen				
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES	PROT	ECTION	SCE- NARIO	ACTIONS/COMMENTS
	(9) Close valve	es G 1 and G3. Open valves (	G6 and G9, and verify that the I	nigh-vacuum a	larm clears.		
No	Skips step.	Plant operator skips this step.	Same as #1-12 when line opened at Step 11.	Low vacuum alarm occurs at Step 11.		5-15	Minor consequence,
art of	Skips closing valves.	Plant operator does not close G1 and G3.  [-HF: valvesclose together and easy to confuse.]	At Step 11 air is introduced into the system, reducing chlorination.	<del>-                                    </del>		5-16	Minor consequence.
	Skips opening valves.	Plant operator does not open G6 and G9. [-HF: same as #5-16.]	Same as #I-1.			5-17	Protection sufficient,
Other than	Wrong valves are opened.	Plant operator opens G5 and G9. [-HF: an% ##5-16.]	Same as #5-15.	Same as #5-15.		5-18	Minor consequence.
		ne serviceman dons the <b>face</b> erify the operation of the per	emask respirator, and operator of sonal protective equipment.	dons <b>self-cont</b> a	ained breathing a	apparatus	s (SCBA). Then
No	Skip step	Neglect to wear the personal protective equipment.	Loss of protection for scenarios where needed.	Observer reminds serviceman of need for personal protective equipment,		5-20	No direct consequence.

HAZOP. WORKSHEFT

'LANT / OPER	ATION: Water Tr	eatment Facility / Procedures		REVIEW DATE: 5/20/93						
.INE/VESSEL	/NODE: Node 5			<b>DRAWING NO.:</b> Procedures for the Change-out of Chlorine Cylinders (see Appendix A)						
DESIGN INTE		g Empty Chlorine Cylinder (w	REVIEW TEAM: F. Leverenz, S. Camp, J. Rude, K. Agee, S. Kanth, K. Murphy, D. Ortiz, J. Angyus, J. Piatt, R. Hansen							
	ras without mean	ingful deviations have been o	J. Platt, N. Ha							
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES	PROTECTION	SCE- NARIO	ACTIONS/COMMENTS				
(11) Slowly disconnect the regulator, check it for leaks, and set it on the floor.										
No	Skip step	Serviceman does not disconnect the regulator.	Hoses could be broken if cylinder is moved at Step 13. Small release; minor irritation,	Observation that regulator is still connected,	5-21	Minor consequences.				
'art of	Skip part of step.	Serviceman does not open slowly while checking for leaks.  [-HF: experience required to judge "slowly" and to differentiate between a leak and residual Cl <sub>2</sub> in the line.]	Loss of protection in previous scenarios,	None,	5-22	No direct consequence.				
As well	Unwanted action	Serviceman drops regulator after disconnect.	Damage regulator; possible "cause" for scenario in reconnection.	Serviceman alerts operations supervisor of drop.	5-23	No direct consequence.				
Other :han	Wrong cylinder	Serviceman selects the wrong cylinder.	Serviceman disconnects in- use cylinder with release of full cylinder contents (see 5-5).  Potential for injuries and fatalities near 315 Building and neighboring buildings.	1) Verify tank valves are closed.  I-HF: procedure doee not require check of cylinder valve   +HF: serviceman has considerable experience].  2) Open slowly with ammonia check.  [-HF: see #5-5, 3, Protection.]  3) Low vacuum alarm and C! <sub>2</sub> alarm.  [-AF: operator may assume thii is normal slarms for disconnect.]	5-24	Sufficient protection.  Existing tagging system to be incorporated into disconnect procedures.				

HAZOP WORKSHEET PAGE B-29

PLANT/OPER	ATION: Water Tr	eatment Facility / Procedures		REVIEW DATE	5/20/93		
.INE/VESSEL				DRAWING NO.:			nge-out of Chlorine x A)
DESIGN INTE	итіон: Removin	g Empty Chlorine Cylinder (w	est cylinder)	REVIEW TEAM:			J. Rude, K. Agee, D. Ortiz, J. Angyus,
Guide Wo	rds without mean	ingful deviations have been o	mitted from this table.		J. Piatt, R. Ha		oraz, o. Angras,
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES	PROT	ECTION	SCE- NARIO	ACTIONS / COMMENTS
	(12) Install t	he cap on the cylinder angle	valve, and install the protective	e hood.			
No	Skip step	Serviceman does not install the cap,	Loss of protection for valves and threads during subsequent handling incidents.	Visual observ	vation when oved (Step 13).	5-25	Low likelihood.
	(13) Position	n the crane and cylinder truck	for loading; open the roll-up	door; remove t	he chocks; and	push tha	cylinder out to the stops.
Reverse	Reverse part of step	Trucks are not in place when cylinder rolled out.	Possibility of vehicle impact with the cylinder resulting in release of C1, Potential injuries in the area.	None.		5-26	Low likelihood.
	(14) Release	e the chain binders, and turn t	the cylinder over to the hoist a	and rigging cre	ew.		
No	Skip step	Chain binders are not released,	Cannot load cylinder onto the truck; potential damage to the equipment.	Hoist crew n chain is conr		5-27	Minor consequence.
	(15) Install	the spreader bar, lift the cylin	der, and place it on the flatbe	d truck.			Note: hoisting and rigging crew has detailed procedure.
Part of	Incomplete installation	Partially hooked,	The dropped cylinder is damaged resulting in a Cl <sub>2</sub> release. Same as #5-26.	Radio for hazmat support.		5-28	Low likelihood.
As well as	Unwanted action	Crane operator mishandles the cylinder lift.	Cylinder strikes object. Same as #5-28.	None. 5-29		5-29	Low likelihood.
Part of	Fails during lift	Crane or rigging fails (broken cables, etc.).	Same as #5-28.	Same as #5-	28.	5-30	Low likelihood. Rigging is certified by non-destructive examination.

PLANT/OPER	ATION: Water T	reatment Facility / Procedures		REVIEW DATE	5120193			
LINE/VESSEL	./NODE: Node 5			DRAWING NO.:	<b>DRAWING NO.:</b> Procedures for the Change-out of Chlorine Cylinders (see Appendix A)			
DESIGN INTENTION: Removing Empty Chlorine Cylinder (west cylinder)  Guide Words without meaningful deviations have been omitted from this table,					REVIEW TEAM: F. Leverenz, S. Camp, J. Rude, K. Agee, S. Kanth, K. Murphy, D. Ortiz, J. Angyus, J. Piatt, R. Hansen			
GUIDE WORD DEVIATION CAUSE CONSEQUENCES					PROTECTION		ACTIONS/COMMENTS	
	(16) Secure th	e cylinder and transport it.						
No	Skip step	Driver does not secure the cylinder.	The cylinder is released during transport (e.g., falls off truck). Potential for cylinder failure, Cl <sub>2</sub> release and injuries to people along the route.			5-31	Low likelihood.	
	(17) Close t	he roll-up door, and exit throu	ugh the walk-through door.					
No	Skip step	Plant operator does not close the doors.	May compromise effectiveness of C1, detectors.	Tour operator	r surveillance,	5-32	Low likelihood.	

Hazard and Operability Study Worksheet

HAZOP WORKSHEFT

LANT/OPER	ATION: Water Tr	eatment Facility / Procedures		REVIEW DATE:	5/21 /93		
INE/VESSEL	/NODE: Node 6			DRAWING NO.: Procedures for the Change-out of Chlorine Cylinders (see Appendix A)			
Suide Wo		eplacement Chlorine Cylinder of the control of the	,	REVIEW TEAM: F, Leverenz, J. Rude, S, Camp, D. Ortiz, J. Angyus, R. Hansen			
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES	PROT	ECTION	SCE- NARIO	ACTIONS/COMMENTS
	(1) Turn on or	verify that the storage room e				Note: Hoisting and rigging crew has detailed procedure.	
Vo	Skip step	Plant operator does not turn the fan on.	Loss of prevention for Step 10 (entry of storage building).	Serviceman notes the fan is off before entry and turns it on.  [—HF: • rvicemm works on many different installations and may not think to check the fan.]		Insignificant consequences.	
	(2) Position the	e crane for unloading,					
Part of	Mis- positioned	Crane is mis-positioned (would require extreme mis-positioning).	Difficulty in moving cylinder to trolley; may delay replacement. It is possible that the cylinder could be damaged, Possible injuries and fatalities in area if release occurs from damage.	Other crew m	nembers,	6-2	Low likelihood. Crane has considerable flexibility.
	(3) Position the	e chlorine transport truck for t	unloading,				
Part of	Mis-positioned	Truck is mis-positioned (would require extreme mispositioning).	Same as #6-2.	Same as #6-	2.	6-3	Low likelihood.

AZOR WORK	SHEET					PAGE &-3		
PLANT/OPER/	ATION: Water Tr	eatment Facility / Procedures		REVIEW DATE: 5/21/93				
LINE/VESSEL	/NODE Node 6			DRAWNG NO.: Procedures for the Change-out of Chlorine Cylinders (see Appendix A)				
<b>DESIGN</b> INTE Guide Wo		eplacement Chlorine Cylinder ingful deviations have been o		REVIEW TEAM: F. Leverenz, J. Rude, S. Camp, D. Ortiz, J. Angyus, R. Hansen				
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES	PROTECTION	SCE- NARIO	ACTIONS/COMMENTS		
	(4) Verify that t	ha chlorine cylinder trolley is	in position to receive the cylin	nder.				
Part of	Mis-positioned	Trolley is mis-positioned and no correction occurs, (The worst case is when the trolley is off the track.)	Same as #6-2.  If it is off the track, it could roll. (The apron or concrete pad is sloped toward parking lot.) It would likely stop when the wheels run off the apron onto the gravel.	Same as #6-2.	6-4	Low likelihood,		
No	(5) Release the	cylinder binder(s) on the tran	Cannot remove the	Hoist and rigging crew	6-5	Minor consequence.		
Part of	Only one binder in place	Driver only releases one binder.	cylinder,  One end of cylinder moves the other does not, same as #6-5.	notice binder at Step 6. Same as #6-5.	6-6	Minor consequence.		
	(6) Install the li	ifting bar, and lift the cylinder			1			
Part of	Incomplete installation	Same as #5-28.	Same as #5-28.	None,	6-7	Low likelihood,		
	(7) Place the cy	linder on the <b>trolley</b> .						
Part of	Fails during lift	Crane or rigging fails (broken cables, etc.).	Same as #5-30.	None,	6-8	Low likelihood, Rigging is certified by non-destructive examination.		
As well as	Unwanted action	Crane operator mis-handles lift.	Same as #5-29.	None,	6-9	Low likelihood.		

							17.102 500
PLANT/OPERA LINE/VESSEL/		eatment Facility / Procedures		REVIEW DATE:  DRAWING NO.:	5/21/93 Procedures for Cylinders (see		nge-out of Chlorine
<b>DESIGN</b> INTE	NTION Install Re	eplacement Chlorine Cylinder	(west cylinder)	REVIEW TEAM:	•	J. Rude, S	S. Camp, D. Ortiz,
Guide Wor	ds without mean	ingful deviations have been o	omitted from this table.		o. Aligyus, it.	i idii 3Cii	
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES	PROTE	CTION	SCE- NARIO	ACTIONS / COMMENTS
	(8) Remove the	lifting bar, removing it from	the immediate area.				
NJo	Skip step	Bar is not removed.	Delay in the replacement of the cylinder.	None,		6-10	Minor consequence.
	(9) Secure the	cylinder to the trolley with ch	nain binders (2).				
Mo	Skip step	Plant operator does not install chain binders.	No consequences except chains dragging as trolley pushed into building.	Sound of drag	ging chains.	6-11	Low likelihood. Primary reason for chain binders as seismic precautions; seismic activity is small (below seismic probability of zone 2).
	(Io) Enter th	ne walk-through door, and op	oen the <b>roll-up</b> door.				
	No meaningful deviations						
	(11) Push th	ne trolley and the chlorine cyl	linder into the building and ag	ainst the rail sto	op. Install the v	vheel cho	ocks.
No	Skip step	Plant operator does not move the cylinder.	Delay in replacement of cylinder.	Position noted staff.	by rest of	6-12	Minor consequences.
Part of	Part of step skipped	Wheel chocks are not installed.	Precaution (against movement) not in place.	Missing chock staff during ro [—HF: chocks ore r as they are under to	utine checks.	6-13	No direct consequence.
	Not positioned	Plant operator does not push the cylinder (on trolley) in far enough.	When the regulator is installed lines are damaged by stretching. Low or no Cl <sub>2</sub> flows to the chlorinator when the cylinder is put in use (see also #I-9).	correction.	nd requires  nis noted when adily reach	6-14	Sufficient protection.

LANT/OPERATION: Water Treatment Facility / Procedures					5121193		
.INE/VESSEL	/NODE: Node 6	•		DRAWING NO,:	Procedures for the Change-out of Chlorine Cylinders (see Appendix A)		
Suide Words without meaningful deviations have been omitted from this table.				F.Leverenz, J. Rude, S. Camp, D. Ortiz, J. Angyus, R. Hansen			
GUIDE WORD	DEVIATION			ECTION	SCE- NARIO ACTIONS / COMMENTS		
	(12) Reques	et the chlorine serviceman to re	emove the protective hood fro	om the chlorine	cylinder.		
No	Skip step	Serviceman does not remove hood.	Delay in replacement.	Noted by star	f,	6-15	
	(13) Observe the rotate t	he position of cylinder angle the cylinder to obtain vertical a	valves. If the valves are not in	n vertical align e chain binder	ment, loosen t s.	he chain l	binders and
No	Skip step	Serviceman does not vertically align the cylinder.  I—HF: alignment done by observation of cylinder connections  I + HF: serviceman has considerable experience with connections.	Potential to for liquid chlorine to enter the ejector and over chlorinate; potential for Cl <sub>2</sub> release from the water.  Release potential unknown.			6-16	Consult the vendor on this scenario and the expected system response. Estimate the amount of C1₂ release potential.
Part of	Part of step	Chains are not tightened after alignment.	No consequence expected.			6-17	No consequence expected.
		e serviceman dons the facema erify the operation of the perso		ons self-conta	ned breathing	apparatus	(SCBA). Then
No	Skip step	Neglect to wear personal protective equipment.	Loss of protection for scenarios where needed.			6-18	No direct consequence.
	(15) Verify t	hat the chlorine cylinder gas a	angle valve is closed.				
No	Skip step	Serviceman does not verify it is closed.	At Step 16, Cl <sub>2</sub> is released when the cap is removed if the valve is not fully closed.  Same as #5-5.	At Step 16, the opened slowd checking for Interpretation of this same mitigat	y while eaks. experienced with	6-19	Sufficient protection.

							FAGE B-30
PLANT/OPER	ATION: Water T	reatment Facility / Procedures		REVIEW DATE:	5/21 /93		
				DRAWING NO.: Procedures for the Change-out of Chlorine Cylinders (see Appendix A)			
DESIGN INTE		Replacement Chlorine Cylinder	REVIEW TEAM: F. Leverenz, J. Rude, S. Camp, D. Ortiz, J. Angyus, R. Hansen			. Camp, D. Ortiz,	
Guide Wo	rds without mear	ningful deviations have been o	mitted from this table.				
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES	PROTECTION		SCE- NARIO	ACTIONS / COMMENTS
	(16) Check	for leaks while slowly removing	g the protective cap from the	cylinder gas a	ngle valve.		
More/ Part of	Too fast/not check	Serviceman opens the cap too quickly or does not check for leaks.  [+ HF: servicemen experienced with importance of this check.]	If valve is open or leaking, the release of $\operatorname{Cl}_2$ is possible (amount depends on valve opening).	Mitigation: Cl emergency re same mitigation	sponse and	6-20	Cause unlikely.
			Same as #5-5.				
No	Skip step	Serviceman does not clean/check sealing surface of angle valve or vacuum regulator,	Possible seal leak at Step 18 or leak from damaged regulator, Cl <sub>2</sub> release at Step 19 same	Leak check a [+HF: serviceme importance of this Mitigation: Cl	t Step 19. n experienced with check.]	6-21	Low likelihood,
			as #5-5,	emergency re same mitigat			
	(18) Install	a new lead seal. Attach the req	gulator to the cylinder gas val	ve, and secure	e it in place by	tightening	g the yoke assembly.
Part of	Incorrect lead seal installation	Serviceman does not install the lead seal or uses the old seal. [+ HF: experienced serviceman knows importance of newseal.]	Same as #6-21,	Same as #6-21.		6-22	Same as #6-21.
Less	Not tight enough	Serviceman does not tighten the yoke assembly enough, [+ HF: serviceman experienced with cylinder yoke attachment. 1	Same as #6-21,	Same as #6-2	21.	6-23	Same as #6-21.
More	Too tight	Serviceman over-tightens the yoke assembly.  I + HF: serviceman experienced with cylinder yoke attachment. ]	Breaks the yoke; replacement of cylinder is delayed.			6-24	Low likelihood.

LANT/OPER	ATION: Water Ti	reatment Facility / Procedures		REVIEW DATE 5/21/93		
INE/VESSEL/NODE: Node 6				Procedures for the Change-out of Chlorine Cylinders (see Appendix A)		
ESIGN INTENTION Install Replacement Chlorine Cylinder (west cylinder)  Guide Words without meaningful deviations have been omitted from this table.			F. Leverenz, J. Rude, S. Camp, D. Ortiz, J. Angyus, R. Hansen			
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES	PROTECTION	SCE- NARIO	ACTIONS / COMMENTS
Other han	Wrong angle valve	Serviceman installs regulator on the liquid valve. [+ HF: servicemen experienced with attachment and must install upside down.]	Same as #6-16.	Same as #6-16.     Tour surveillance notices regulator upside down.	6-25	Low likelihood.
	(19) Check	for leaks. <b>Slowly</b> open the chlo	orine cylinder gas supply valv	e.		
'art of	Not check for leaks	Serviceman does not check for leaks.	Loss of protection in previous scenarios.		6-26	No direct consequence.
Vlore	Opens too fast	Serviceman opens valve too fast.	Releases more chlorine than necessary for leak detection.	None.	6-27	Low likelihood.
			No health effects expected.	Personal protective equipment for serviceman and operator.		
	(20) Adjust	the cylinder weight scale to in	dicate 2,000 pounds of produ	ct available in the cylinder.		
	No meaningful deviations					
	(21) Open s	ystem supply valves G-1 and	G-5.			
No or 'art of	Skip step or part of the step	Plant operator does not open the valves.	Replacement chlorine not available; loss of chlorination. Same as #I-1.	1) High vacuum alarm. 2) Residual C1, surveillance checks (see also #1-1, Protection 3).	6-28	Sufficient protection.
_ess	Not opened completely	Plant operator does not open one or both of the valves completely.	No consequence.		6-29	
Other than	Wrong valve selected	Plant operator opens the G3 valve instead of the G 5 valve.  [-HF: several valves in one location.]	Draws Cl <sub>2</sub> from both cylinders at the same time. Potential for loss of chlorination (see #1 -1).	Surveillance checks weight of cylinders.     Surveillance checks rate indicators on regulators.	6-30	Minor consequences.

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LANT/OPERA	ATION: Water Tr	eatment Facility / Procedures		REVIEW DATE:	5/21/93		
INE/VESSEL/I	NODE: Node 6			DRAWING NO.:			nge-out of Chlorine
)ESIGN INTEN	NTION: Install R	eplacement Chlorine Cylinder	(west cylinder)	REVIEW TEAM:	Cylinders (see F, Leverenz, J. J. Angyus, R. I	Rude, S	x A) S. Camp, D. Ortiz,
<b>Buide</b> Work	ds without mean	ingful deviations have been o	mitted from this table,				
GUIDE WORD	DEVIATION	CAUSE	CONSEQUENCES	PROT	ECTION	SCE- NARIO	ACTIONS/COMMENTS
	(22) Record in the log book the chlorine cylinder identification number and the scale weight.						
	No meaningful deviations						
	(23) Report	any deficiencies to the superv	risor for initiation of necessary	corrective ac	tion.		
<b>7</b> 0	Skip step	Notification not made.	Delay in completing action.			6-31	Minor consequences,
	(24) Notify the Hanford Fira Department and the 364 Powerhouse that the chlorine cylinder change-out activities are complete.						
No	Skip step	Notification not made.	No consequence.			6-32	Minor consequence.
(25) Close the roll-up door, and axit through the walk-through door.							
	No meaningful deviations						

Hazard ma Uperability Study Worksheet

# APPENDIX C ESTIMATING THE EFFECTS OF CHLORINE RELEASES

## APPENDIX C: ESTIMATING THE EFFECTS OF CHLORINE RELEASES

Information contained in this appendix was excerpted, with permission, from Estimating the Area Affected by a Chlorine Release (The Chlorine Institute, 1991). The computer dispersion model used by The Chlorine Institute to generate release scenarios was based on generic industrial accidents and atmospheric conditions. The results depend on the atmospheric conditions and wind speeds assumed for the releases as well as on the terrain. They serve as an aid to estimating the range of potential consequences of chlorine releases. The HAZOP study team used this reference for the release and dispersion of chlorine to understand the potential consequences and impacts of releases.

#### C.1 Characteristics of Chlorine Releases

Unintended chlorine **releases** have occurred as a result of industrial accidents involving equipment such as tanks, pipelines, relief valves, and vents.

Chlorine releases can be modeled as either instantaneous puff releases or continuous releases. During an instantaneous release, such as a cylinder rupture, large amounts of chlorine are released in a relatively short period of time. In a continuous release, such as the **failure** of a gasket, the chlorine release rate is maintained over a period of time until it is controlled or until the cylinder is depleted.

Initially, during a cylinder release, either gaseous or liquid chlorine, or both, may be released. As a result of the release, the pressure and temperature in the cylinder decreases, slowing the release rate. Upon release, pressurized liquid chlorine cools to its boiling point (-29°F) and boils off. Mixing with the atmosphere is delayed because the liquid must first evaporate. Chlorine vapors, however, mix immediately. If released under pressure, liquid chlorine can flash to a vapor, resulting in a two-phased jet release.

During the intermediate phases of a chlorine release, the chlorine is most influenced by atmospheric conditions. It continues to mix with the air and with moisture in the air. Depending on atmospheric conditions, aerosols may form. Eventually, a dense gas plume forms. This heavier-than-air plume remains at ground level as it moves downwind until, through dilution, its density equals the density of air.

Because of the atmospheric variability, stability classes are used to predict the dispersion of the plume. In the early morning, the atmosphere is stable. Daytime solar heating creates air movement and an unstable atmosphere. Atmospheric stability classes range from "very unstable" **Class** A to "very stable" Class G. Dispersion is also affected by the wind, the mixing height, and the terrain.

#### **C.2** Chlorine Release Scenarios

The consequences of the accident scenarios **identified** during the HAZOP study can be categorized as:

- Chlorine cylinder releases
- Process line breaks and releases
- Process equipment leaks.

The potential accident scenarios are identified in the HAZOP Study Worksheets (Appendix B).

To estimate the potential consequences and impacts of these accidents, release scenarios were **selected** from **Estimating** the Area **Affected** by a Chlorine Release. The scenarios are based on typical industrial accidents with conservative modeling assumptions. Five **accident** scenarios were selected for consideration:

- 1. A 1-ton cylinder is struck and its liquid valve is sheared off, resulting in the release of liquid chlorine.
- 2. Half-inch tubing is sheared off and chlorine gas is released (modeled with infinite supply).
- **3.** A 1-inch pipe is sheared off and chlorine gas is **released** (modeled with infinite supply).
- 4. Half-inch tubing is sheared off and liquid chlorine is released (modeled with infinite supply).
- **A** l-inch pipe is sheared off and liquid chlorine is released (modeled with infinite supply).

The assumptions for these five release scenarios are

- Three-foot release height
- Ambient air temperature of 68°F
- Ambient relative humidity of 50 percent
- Liquid or gaseous chlorine at 68°F
- Changes in ambient temperature or relative humidity assumptions have little **effect** on dispersion. Changes in assumptions about temperature and pressure of chlorine prior to release **can** significantly **affect** dispersion.

- Five-mile-per-hour wind speed. Because ambient concentration is inversely proportional to wind sped, concentrations can reconverted to other wind conditions by dividing 5 miles per hour by the actual wind speed and multiplying the result by the concentration.
- Average wind fluctuation of approximate] y 5°. If wind shifts are greater, the area impacted by the plume is greater.
- Stability Classes:
  - Stability Class B: Strong and moderate solar radiation with low wind speed. Occurs during the day, generally in the mornings, with clear skies and wind speed less than 10 miles per hour.
  - -- Stability **Class** F: Occurs at night, with wind sped less than 6 miles per hour, and with less than 40 percent cloud cover.
  - -- Stability **Class** D: Used when classes B and F are not applicable.

#### C.3 Predicted Chlorine Consequences

Figures C-1 through C-5 show graphically the areas potentially affected by chlorine releases for five generic accident scenarios\*. Downstream distances are depicted at which chlorine concentrations exceed 25 parts per million (ppm) and 10 ppm.

The dispersion distances and downwind concentrations of chlorine resulting from the scenario **modelling** are summarized in Table C-1. The **25-ppm** chlorine concentration is the immediately-dangerous-to-life-or-health (**IDLH**) level for chlorine, and 10 ppm is **40** percent of the **IDLH**. Ten ppm was chosen as a reference point for emergency planning because of the uncertainty in dispersion modeling.

<sup>\*</sup> The graphs in Figures C-1 through C-5 are truncated on the right-hand side of the x-axis. In fact, these curves extend to meet the x-axis. Limitations in display prevented the full extension from being shown.

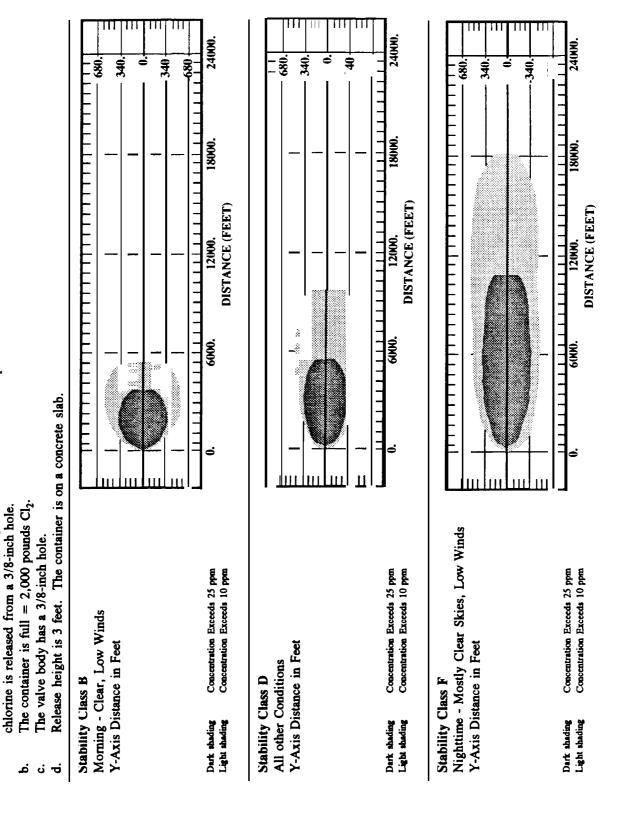
## **2.4** Potential Impacts of Chlorine Releases at the Hanford 300-Area Water Treatment Facility

If a large chlorine release occurs from the Hanford 300-Area Water Treatment Facility, wind from the northwest, west, and southwest would disperse it across the Columbia River to the residences on the far side, more than 3/4 of a mile away. In addition, boaters on the river and any workers occupying the pump house would also likely be exposed. The pump **house**, however, is normally unoccupied.

Wind from the north would carry a large chlorine plume to the 337 Office Building, resulting in the potential exposure of its more than 300 occupants. Small releases of chlorine would probably result in minor irritations to workers in the **area**.

Table C-1. Summary of Dispersion Distances and Downwind Concentrations for Chlorine Release Scenarios

Scenario Description	Stability Class B Distance in feet and miles		Distai	Class D nce <b>in</b> d miles	Stability Class F Distance in feet and miles		
•	25 ppm	10 ppm	25 ppm	10 ppm	25 ppm	10 ppm	
1) A 1-ton cylinder is struck and its liquid valve is shared off. Liquid chlorine is released from a 3/8-inch hole.	3,600 0.7	<b>5,400</b> 1.0	<b>5,400</b> 1.0	9,600 1.8	10,800 2.0	18,000 3.4	
2) Half-inch, type-K copper tubing is sheared off. Chlorine gas is released (modeled with infinite supply).	800	1,200	1,200	2,100	1,800	3,300	
	0.2	0.2	0.2	0.4	0.3	0.6	
3) A 1-inch schedule-80 pipe is sheared off. Chlorine gas is released (modeled with infinite supply).	1,600	2,800	2,600	<b>4,400</b>	<b>4,200</b>	<b>7,400</b>	
	0.3	0.5	0.5	0.8	0.8	1.4	
4) Half-inch, type-K copper tubing is sheared off. Liquid chlorine is released (modeled with infinite supply).	2,000	3,750	3,000	5,500	5,250	9,250	
	0.4	0.7	0.6	1.0	1.0	1.8	
5) A l-inch schedule-80 pipe is sheared off. Liquid chlorine is released (modeled with infinite supply).	4,000	7,000	7,000	7,000	11,000	18,500	
	0.8	1.3	1.3	2.0	2.0	3.5	



A 1-ton cylinder is struck and its liquid valve is sheared off. Liquid

Scenario Description:

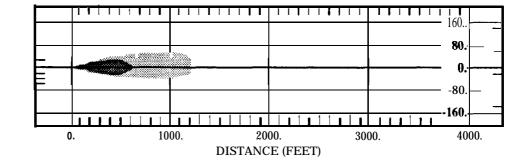
Figure C-1. One-Ton Liquid Chlorine Release from Sheared-off Valve

#### scenario Description:

- **a.** Half-inch, type-K copper tubing is sheared off. Chlorine gas is released (modeled with infinite supply).
- b. Release height is 3 feet.

#### Stability Class B

Morning - Clear, Low Winds Y-Axis Distance in Feet

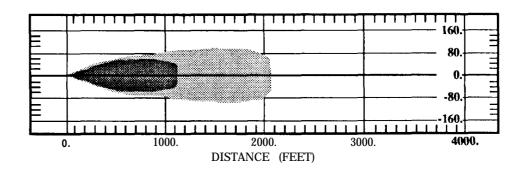


Dark shading Light shading

Concentration Exceeds 25 ppm Concentration EXCEEdS 10 ppm

#### Stability Class D

All other Conditions Y-Axis Distance in Feet



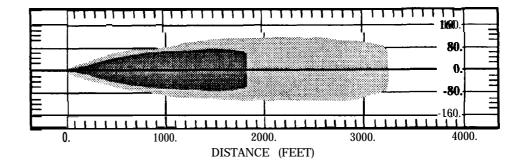
Dark shading Light shading Concentration Exceeds 25 ppm Concentration Exceeds 10 ppm

#### Stability Class F

Nighttime - Mostly Clear Skies, **Low** Winds Y-Axis Distance in Feet



Concentration Exceeds 25 ppm Concentration Exceeds 10 ppm

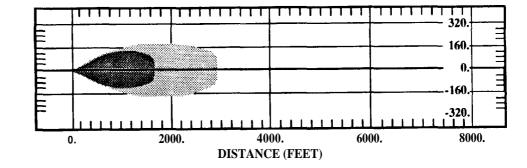


#### **Scenario Description:**

- **a.** A 1-inch, schedule-80 pipe is sheared off. Chlorine gas is released (modeled with **infinite** supply).
- b. Release height is 3 feet.

#### Stability Class B

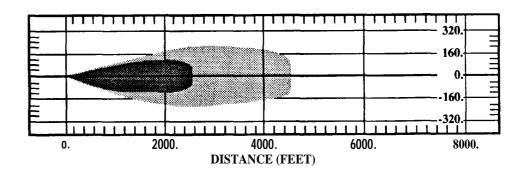
Morning - Clear, Low Winds Y-Axis Distance in Feet



Dark shading Light shading Concentration Exceeds 25 ppm Concentration Exceeds 10 ppm

#### Stability Class D

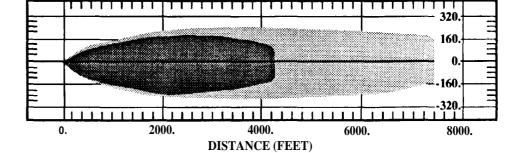
**All** other Conditions Y-Axis Distance in Feet



Dark shading Light shading Concentration Exceeds 25 ppm Concentration Exceeds 10 ppm

#### Stability Class F

Nighttime - Mostly Clear Skies, **Low** Winds Y-Axis Distance in Feet



Dark shading Light shading Concentration Exceeds 25 ppm Concentration Exceeds 10 ppm

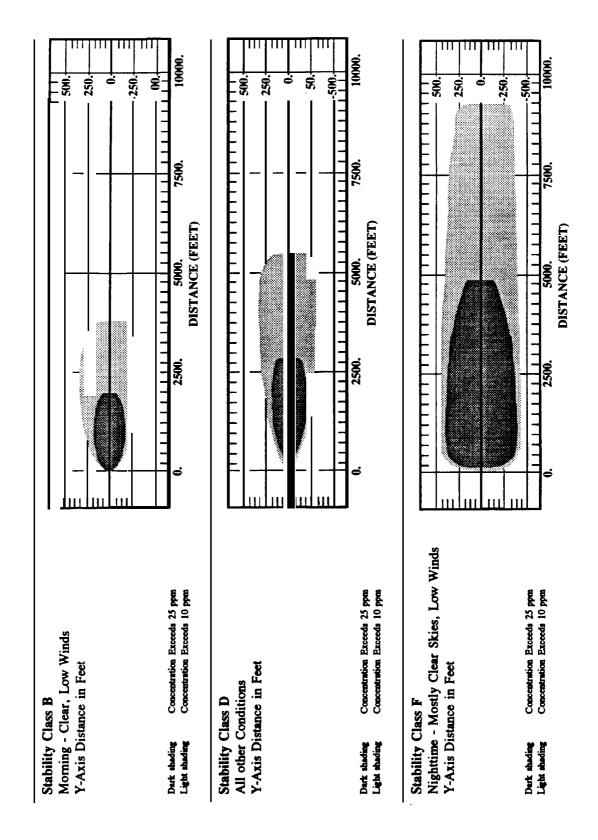


Figure C-4. Liquid Chlorine Release from Sheared-off 1/2-inch Tubing

Half-inch, type-K copper tubing is sheared off. Liquid chlorine is

released (modeled with infinite supply).

Scenario Description:

Release height is 3 feet,

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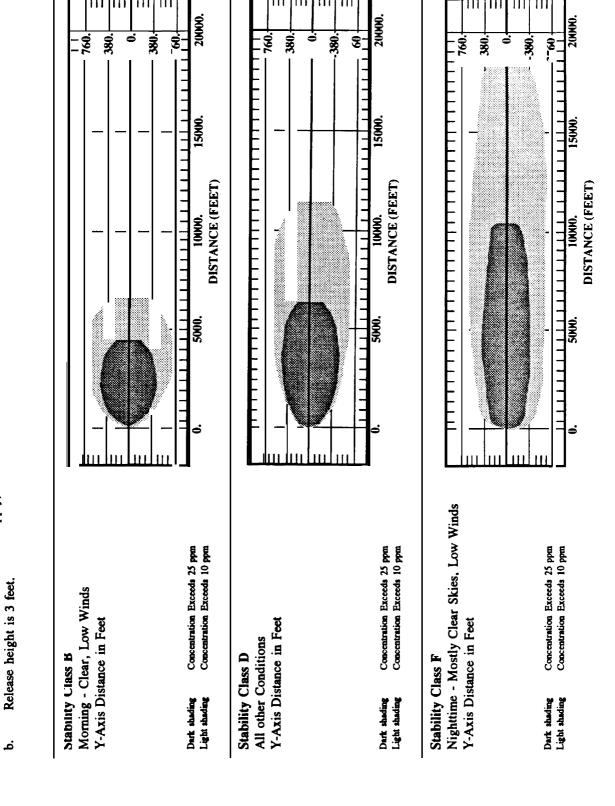


Figure C-S. Liquid Chlorine Release from I-inch Pipe Break

A 1-inch, schedule-80 pipe is sheared off. Liquid chlorine is

Scenario Description:

released (modeled with infinite supply).

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### APPENDIX D

## MATERIAL SAFETY DATA SHEET FOR CHLORINE

## APPENDIX D: MATERIAL SAFETY DATA SHEET FOR CHLORINE\*

SECTION 1: CHEMICAL PRODUCTS& COMPANY IDENTIFICATION							
Occupational Health Services, Inc. 11 West 42nd Street, 12th Floor New York, New York 10036 1-800-445-MSDS (1-800+5-6737) 1-212-789-3535	For Emergency Source Information Contact: 1-615-366-2000						
Substance: Chlorine	CAS <b>Number:</b> 7782-50-5 RTECS <b>Number:</b> FO2100000						
	<b>Molecular;</b> Chlorine Mol.; <b>Diatomic</b> Chlorine; Dichloride; Molecular STCC 4904120; UN 1017 <b>CL2</b> ; 0HS04600						
Chemical Family: Halogen	Inorganic Gss						
SECTION 2: COM	SECTION 2: COMPOSITION/INFORMATION OF INGREDIENTS						
Component: Chlorine	CAS Number: 7782-50-5						
Percentage: 100.0	Other Contaminants: None						
SECTION 3: HAZARDS IDENTIFICATION							
CERCLA Ratings (Scale O-3): Health=3 Fire=0 Reactivity=O Persistence=O NFPA Ratings (Scale 0-4): Health=3 Fire=0 Reactivity=O							
Emergency Overview: Chlorine is a <b>greenish-yellow gas with a strong odor. Harmful if inhaled. Causes respiratory tract, skin,</b> and eye burns. Container may rupture in heat or fire. May ignite combustibles. Do not breathe gas. Do not get in eyes, on skin, or on clothing. Keep away from heat and flame. Store away from combustible materials. Do not puncture container. Keep <b>container</b> tightly closed. Wash thoroughly <b>after</b> handling. Use ordy with adequate ventilation.							
Potential <b>Health</b> Effects:							
Short Term Exposure: May cause sores, frostbite, runny nose, sneezing, paleness, hoarseness, tearing, blurred vision, drooling, bloody spit, stomach pain, coughing, difficulty breathing, lung damage, bluish skin color, suffocation, weakness, headache, anxiety, restlessness, dizziness, irregular heartbeat, heart failure, collapse, and shock. May also cause death.							
carcinogen status: OSHA:	Long Term Exposure: May cause skin sores, acne, tooth decay, and lung effects.						
NTP:	N N N						

<sup>\*</sup> Adapted by permission of Occupational Health Services, Inc.

#### **SECTION 4: FIRST AID MEASURES**

- Inhalation: First Aid Remove from exposure area to fresh air immediately. If breathing has stopped, give artificial respiration. Maintain airway and blood pressure and administer oxygen if available. Keep affected person warm and at rest. Treat symptomatically and supportively. Administration of oxygen should be performed by qualified personnel. Get medical attention immediate y.
- Skin Contact: First Aid Remove contaminated clothing and shoes immediately. Wash affected area with soap or mild detergent and large amounts of water until no evidence of chemical remains (at least 15-20 minutes). In case of chemical bums, cover area with sterile, dry dressing. Bandage securely, but not too tightly. Get medical attention immediately.
- Eye Contact: Firat Aid Wash eyes immediately with large amounts of water, occasionally lifting upper and lower lids, until no evidence of chemical remains (at least 15-20 minutes). Continue irrigating with normal saline until the pH has returned to normal (30-60 minutes). Cover with sterile bandages. Get medical attention immediately.
- Ingestion: First Aid Do not use gastric lavage or emesis. Dilute the acid immediately by drinking large quantities of water or milk. If vomiting persists, administer fluids repeatedly. Ingested acid must be diluted approximately 100 fold to render it harmless to tissuea. Maintain airway and treat shock (Dreisbach, handbook of poisoning, 12th cd.). Get medical attention immediately. If vomiting occurs, keep head below hips to help prevent aspiration.

Note to physician:

Antidote: No specific antidote. Treat symptomatically and supportively.

#### **SECTION 5: FIRE FIGHTING MEASURES**

Fire and Explosion Hazard: Negligible fire hazard when exposed to heat or flame.

- Oxidizer: Oxidizers decompose, especially where heated, to yield oxygen or other gases which will increase the burning rate of combustible matter. Contact with easily oxidizable, organic, or other combustible materials may result in ignition, violent combustion or explosion.
- Extinguishing Media: Water only, no dry chemical, carbon dioxide or halon (1990 Emergency Response Guidebook, DOT P 5800.5). For larger fires, use water spray or fog (1990 Emergency Response Guidebook, DOT P 5800.5).
- **Firefighting:** Move container from fire area if you can do it without risk. Apply cooling water to sides of containers that are exposed to flames until **well** after fire is out. Stay away from enda of tanks. For massive fire in cargo area, use unmanned hose holder or monitor nozzles; if this is impossible, withdraw from area and let fire bum. For small fires, contain and let bum; if fire must be fought, water spiny or fog is recommended (1990 Emergency Response Guidebook, DOT P 5800.5, guide page 20).

Extinguish using agents suitable **for** type of fire. Cool containers with flooding amounts of water, **apply** from as **far** a **distance** as possible. Avoid breathing poisonous vapors, keep upwind. Evacuate to a radius of 2,500 feet if material is leaking.

Hazardous Combustion products: Thermal decomposition products may include toxic and corrosive fumes of chlorine,

#### **SECTION 6: ACCIDENTAL RELEASE MEASURES**

Occupational Spill: Stop leak if you can do it without risk. Keep combustibles away from spilled material. Keep **unnecessa**ry people away; isolate **area** and deny entry until gas has dispersed. **Ventilate** closed spaces before entering.

Reportable Quantity (RQ): 10 pounds

The Superfund Amendments and Reauthorization Act (SARA) Section 304 requires that a release equal to or greater than the reportable quantity for this substance be immediately reported to the **local** emergency planning committee and the state emergency response commission (40 **CFR** 355.40). If the release of this **substance** is reportable under **CERCLA** Section 103, the National Response Center must be notified immediately at (800) 424-8802 or (202) 426-2675 in the metropolitan Washington, DC, area (40 **CFR** 302.6).

**Soil** Spill: Dig a pit, pond, lagoon or holding area to contain liquid or solid material. Dike surface flow using soil, sandbags, foamed polyurethane or foamed concrete. Absorb bulk liquid with fly ash or cement powder. Add caustic soda.

Air **Spill:** Apply water spray to knock down and reduce vapors. Knockdown water is corrosive and toxic and should be **diked** for containment and later disposal.

Water Spill: Neutralize with caustic soda.

If Dissolved, at a concentration of 10 ppm or greater, apply activated carbon at ten times the amount that has been spilled.

Use mechanical dredges or lifts to extract immobilized masses of pollution and precipitates.

#### SECI'10N 7: HANDLING AND STORAGE

Storage: Observe **all** federal, state and local regulations when storing or disposing of this substance. For assistance, contact the district director of the environmental protection agency.

Protect against physical damage. Separate from combustible, organic or easily oxidizable materials and especially isolate from acetylene, ammonia, hydrogen, hydrocarbons, ether, turpentine, and **finely** divided metals. Store outdoors or in a well-ventilated, detached or segregated areas of noncombustible instruction **(NFPA** 49, **Hazardous** chemicals Data, 1975).

Store away from incompatible substances.

Consult NFPA Publication 43C, Storage of Gaseous Oxidizing Materials, for storage requirements.

Threshold Planning Quantity (TPQ): The Superfund Amendments and Reauthorization Act (SARA)

Section 302 requires that each **facility** where any extremely hazardous substance is present in a
quantity **equal** to or greater than the **TPQ** established for that substance notify the state emergency
response commission for the state in which it is **located**. Section 303 of SARA requires these **facilities** to participate in local emergency response planning (40 **CFR** 355.30).

#### SECTION 7: HANDLING AND STORAGE (continued)

Threshold Quantity (TQ): 1,500 pounds

The **Occupational** Safety and Health Administration **(OSHA)** process safety management **(PSM)** standard requires that facilities using a process that involves a chemical at or above its specified threshold quantity comply with the provisions of 29 **CFR** 1910.119, process Safety Management of Highly Hazardous Chemicals.

#### SECTION 8: EXPOSURE CONTROLS/PERSONAL PROTECTION

#### **Exposure Limits:**

#### Chlorine:

0.5 ppm (1.5 mg/m³) OSHA TWA; 1 ppm (3 mg/m³) OSHA STEL 0.5 ppm (1.5 mg/m³) ACGIH WA: 1 ppm (3 mg/m³) ACGIH STEL 0.5 ppm (1.5 mg/m³) NIOSH recommended TWA;

1 ppm (3 mg/m³) NIOSH recommended STEL 0.5 ppm (1.5 mg/m³)DFG MAK TWA;

1 ppm (3 mg/m<sup>3</sup>) DFG MAK 5 minute peak, Momentary Value, 8 times/shift

Measurement Method: Bubbler; lon-Specific electrode; (OSHA # 1D101).

100 pounds SARA Section 302 Threshold Planning Quantity

10 pounds SARA section 304 Reportable Quantity

10 pounds CERCLA Section 103 Reportable Quantity

1,500 pounds OSHA Process Safety Management Threshold Quantity

Subject to SARA Section 313 Annual Toxic Chemical release reporting.

NOTE: OSHA limits adopted January 19, 1989 are subject to the decision of the 11th Circuit

Court of Appeals (AFL-CIO V. OSHA) as of July 7, 1992.

Ventilation: Provide local exhaust or process enclosure ventilation to meet published exposure limits.

**Eye Protection:** Employee must **wear** splash-proof or dust-resistant **safety goggles** and a **faceshield** to prevent contact with this substance.

Emergency Wash Facilities: Where there is any possibility that an employee's eyes and/or skin

may be exposed **to** this substance, the employer should provide an eye wash fountain and quick drench shower within the immediate **work** area for emergency use.

Clothing: Employee must wear appropriate protective (impervious) clothing and equipment to prevent any possibility of skin contact with this substance.

Gloves: Employee must wear appropriate protective gloves to prevent contact with this substance.

**Respirator:** The following respirators and maximum use concentrations are recommendations by the U.S. Department of Health and Human Services, N1OSH Pocket Guide to Chemical Hazards; N1OSH criteria documents or by the U.S. Department of Labor, 29 <u>CFR</u> 1910 Subpart Z.

The specific respirator selected must be based on contamination levels found in the work place, must not exceed the working limits of the respirator and be jointly approved by the National Institute for Occupational Safety and Health and The Mine Safety and Health **Administration** (N1OSH-MSHA).

#### SECTION 8: EXPOSURE CONTROLWPERSONAL PROTECTION(continued)

#### Chlorine:

**5 ppm – Arty** chemical cartridge respirator with cartridge(s) providing protection against chlorine. Any supplied-air **respirator**. Any self-contained breathing apparatus.

**12.5 ppm** — .4ny supplied-air respirator operated in a continuous-flow mode. Any powered, air-purifying **respirator** with cartridge(s) providing protection against chlorine.

**25 ppm** — Any self-contained breathing apparatus with a full facepiece. Any supplied-air respirator with a full facepiece. Any air-purifying, full-facepiece respirator (gas mask) with a chin-style, front- or back-mounted canister providing protection any powered, air-purifying respirator with a tight-fitting facepiece. Any cartridge(s) providing protection against chlorine. Any chemical cartridge respirator with a full facepiece and cartridge(s) providing protection against chlorine.

**30 ppm – Any** supplied-air respirator that has a **full facepiece** and **is** operated in a **pressure-demand** or other Positiv-pressure mode.

**Escape** — any air-purifying, **full-facepiece** respirator (gas mask) with a chin-style, front- or back-mounted canister providing protection against chlorine. Any appropriate **escape-type**, self-contained breathing apparatus.

#### For Firefighting and Other Immediately Dangerous to Life or Health Conditions:

Any self-contained breathing apparatus that has a **full facepiece** and is **operated** in a **pressure-demand** or other **positive-pressure** mode.

Any supplied-air respirator that has a full facepiece and is operated in an pressure-demand or other positive-pressure mode in combination with an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive-pressure mode.

#### SECTION 9: PHYSICAL AND CHEMICAL PROPERTIES

Description:	Pale greenish-yellow gas with a characteristic, suffocating odor.	Molecular Weight: 70.906		
Molecular Fo	ormula: Cl <sub>2</sub>	Boiling Point: -3 l°F (-35°C)		
Melting <b>Point</b>	: <b>—150°F</b> (–101°C)	Vapor Pressure (mm Hg): 5168 mm Hg @ 21°C		
Vapor Densit	y (Air = I): 2.49	Specific Gravity (water = 1): 3.214 grams/liter @ 0°C		
Water Solub	ility: 1.46% @0°C	Odor Threshold: 0.01 ppm		
Solvent <b>Solub</b>	ility: Soluble in alkalies.			

#### **SECTION 10: STABILITY AND REACTIVITY**

Reactivity: Stable under normal temperatures and pressures.

Conditions to Avoid: Avoid contact with combustible materials (wood, paper, oil, etc); contact may result in ignition or explosion. Material may be poisonous; avoid inhalation of vapors or contact with skin. Do not allow material to contaminate water sources.

#### Chlorine Incompatibilities:

Acetylene Explosive reaction

Alcohols: Formation of explosive alkyl hypochlorites.

Alkyl Isothiourea Salts: Formation of explosive nitrogen trichloride.

Ammonia: Explodes when heated.

**Antimony**: Ignition reaction

Arsenic: Spontaneous ignition.

N-Arykulfinamides: Possible violent reaction.

Benzene: Explosive reaction catalyzed by light

**Boron:** Ignites on contact.

Bromine Pentafluoride: Explosive reaction.

Calcium Chlorite: Forms explosive chlorine dioxide.

Calcium Nitride: Incandescent reaction.

Carbon (activated): Ignites on contact.

Carbon disulfide: Explosive reaction in the presence of iron catalyst.

Cesium Nitride: Attacked by chlorine.

3-Chloropropyne: Possible explosion.

Chromyl Chloride + Carbon: Possible explosion.

**Combustible Materials:** Contact with the liquid is likely to result-in an explosion. Contact with the gas may result in ignition or an explosion.

Diborane: Explodes on contact at ambient temperatures.

Dichloromethylarsine: Possible explosion.

Diethyl Ether: Explodea.

Diethylzinc: Ignition.

Dimethylformamide: Explosion hazard.

Dimethyl Phosphoramidate: May form explosive nitrogen trichloride.

Dioxygen Difluoride: Ignition or explosive reaction.

**Disilyl Oxide**: Explosive reaction.

4,4' — Dithiodimorpholine: May form explosive compound.

**SECTION 10: STABILITY AND Reactivity (continued)** 

**Ethylene:** Explosive reaction in the presence of light or catalysts.

Ethylene I mine: Formation of explosive -chloroethylene imine.

Ethylphosphine: Explosion on contact.

**Flammable** compounds: Contact with the liquid is **likely** to **result** in an explosion. Contact with the gas may result in ignition or an explosion.

Fluorine: Ignition followed by explosion on sparking.

Hexachlorodisilane: Ignition above 200° C with possible explosion.

Hydrazine: Ignition reaction.

**Hydrocarbons:** Contact with the liquid ia likely to result in an explosion. Contact with the gas may result in ignition or an explosion. Addition of a Lewis acid to **chlorine-hydrocarbon** mixtures will **result** in the release of large **volumes** of **hydrogen** chloride.

**Hydrogen:** Explosive mixtures.

**Hydrogen** Peroxide + Potassium **Hydroxide**: Luminescent reaction.

Hydroxylamine: Spontaneous ignition.

**Iodine:** Violent reaction.

Iron Carbide: Incandescent reaction.

Lithium Silicide: Incandescent reaction when heated.

Metals and Alloys: Ignition on contact; some metals may be corroded in the presence of moisture.

Metal Acetylides: Ignition Reaction.

Metal **Hydrides**: Ignition.

Metal Oxides: Vigorous reaction and possible ignition.

Metal Phosphides: Ignition.

Nitrogen Compounds: May form explosive nitrogen trichloride.

Nitrogen Triiodide: Explosive reaction on contact.

Non-Metal Hydrides: Ignite on contact.

Oxygen: Explosion on heating.

Oxygen Difluoride: Explodes on warming.

Phenylmagnesium Bromide: Possible explosion.

Phosphorous: Explosive reaction on contact with the liquid; ignition on contact with the gas.

**Phosphorous Compounds:** Ignition.

Phosphorous Isocyanate: Vigorous reaction.

Polychlorobiphenyl: Exothermic Reaction.

(Poly) Oxomonosilane: Ignition.

Potassium Halides: Ignition.

#### **SECTION 10: STABILITY AND REACTIVITY (continued)**

Sin: Ignite-s on contact with gaseous chlorine at ambient temperatures.

Sines: Possible explosion on heating.

**Sodium Hydroxide:** Violent reaction.

Stannous Fluoride: Reaction occurs with flaming.

**Stibine**: Explosive reaction if heated.

Sulfamic Acid: May form explosive nitrogen trichloride.

Sulfides: Ignition.

Tellurium: Incandescent reaction.

Tetramethyldiirsine: Spontaneous ignition.

Tetramethylsilane: Possible explosion in presence of a catalyst.

Tetraselenium Tetranitride: Explosion on contact.

Trialkylboranes: Ignition reaction.

Trimethyl Thionophosphate: Possible explosion.

Vanadium (Powder): Explosion on contact with the liquid.

Hazardous Decomposition: Thermal decomposition products may include toxic and corrosive fumes of chlorine.

**Polymerization**: Hazardous polymerization has not been **reported** to occur under normal temperatures and **pressures**.

#### **SECTION 11: TOXICOLOGY INFORMATION**

Chlorine Toxicity Data: 2530 mg/m³/30 minutes inhalation-human LC<sub>LO</sub>; 500 ppm/5 minutes inhalation-human LC<sub>LO</sub>; 293 ppm/1 hour inhalation-rat LC<sub>50</sub>; 137 ppm/1 hour inhalation-mouse LC<sub>50</sub>; 660 ppm/4 hours inhalation-rabbit LC<sub>LO</sub>; 330 ppm/7 hews inhalation-guinea pig LC<sub>LO</sub>;800 ppm/30 minutes inhalation-dog LC<sub>LO</sub>; 660 ppm/4 hours inhalation-eat LC<sub>LO</sub>; 500 ppm/5 minutes inhalation-mammal LC<sub>LO</sub>; mutagenic data (RTECS); reproductive effects data (RTECS).

Carcinogen Status: None.

**Local Effects:** Corrosive – Inhalation, skin, eye.

Acute toxicity Level: Toxic by inhalation.

Target Effects: Poisoning may affect the lungs.

At Increased Risk from Exposure: Persons with pm-existing heart disease or tuberculosis.

#### **SECTION 11: TOXICOLOGY INFORMATION (continued)**

Health Effects:

Inhalation of Chlorine: Corrosive/Toxic

30 ppm immediately dangerous to life or health.

**Acute Exposure** – Mucous membrane irritation may **occur** at 0.2 to 16 ppm and cough at 30 ppm. Inhalation of 500 ppm for 5 minutes has been **lethal** in humans and 1,000 ppm may be fatal after a few deep breaths. Occupational exposures have resulted in burning of the nose and mouth with **rhinorrhea**, respiratory distress **with** coughing, choking, wheezing, mica, **retching**, hemoptysis, **substernal** pain, **dyspnea**, and cyanosis. **Tracheobronchitis**, progressing to immediate or possibly delayed **pulmonary** edema and occasional **pneumonitis** have also been reported. Cough generally increases in frequency **and** severity **after** 2 to 3 days and became productive of thick **mucopurulent** sputum, which disappears by the end of 14 days. Lung damage is usually not permanent; respiratory distress usually subsides within 72 hours. At high concentrations, **chlorine** may act as an asphyxiant by causing cramps of the larynx muscles and **swelling** of the mucous membranes. other symptoms may include salivation, anxiety, sneezing, pallor or redness of the face, weakness, hoarseness, headache, dizziness, and general excitement and restlessness. Massive inhalation may also cause death by cardiac **arrest**.

Chronic Exposure — Persons repeatedly exposed to low concentrations may develop **chloracne**, olfactory deficiency and tolerance build-up. prolonged and **repeated** exposure to 0.8- 1.0 ppm may cause permanent, although moderate reduction in pulmonary function. Chronic exposure at 5 ppm may result in inflammation of the mucous membranes of the nose, disease of the bronchi, and increased susceptibility to respiratory infection including tuberculosis. Dental erosion may occur. Animals surviving sublethal exposures for 15 to 193 days alter gassing showed marked emphysema.

#### **Skirt Contact:**

Chlorine: Corrosive.

**Acute Exposure** — High vapor concentrations may irritate the skin and cause burning and pricking sensations, inflammation, and vesicle formation. Contact with liquid may **cause** burns, blistering, tissue **destruction**, and frostbite.

**Chronic Exposure – Effects** depend on the concentration and duration of exposure **Repeated** or prolonged **contact** may result in dermatitis or effects similar to acute exposure.

#### **Eye Contact:**

Chlorine: Corrosive.

**Acute Exposure** – Exposure to concentrations of chlorine gas as low as **3-6** ppm may **cause** redness, pain, **blurred** vision, and **lacrimation**. Direct **contact** with liquid may cause bums. Chlorine dissolved in water, and **placed** into the anterior chambers of rabbit eyes caused severe inflammation, **corneal** opacity, iris atrophy and injury to the lens.

Chronic Exposure – Effects depend on the concentration and duration of exposure. Repeated or prolonged exposure may cause conjunctivitis or effects as in acute exposure.

#### Ingestion of Chlorine:

**Acute Exposure** – Ingestion of a gas is very unlikely. Ingestion of the liquid may cause bums of the lips, mouth and mucous membranes of the **gastrointestinal** tract, possible ulceration or perforation, abdominal pain, **tachycardia**, prostration and **circulatory** collapse.

Chronic Exposure - No data available.

#### **SECTION 12: ECOLOGICAL INFORMATION**

Environmental Impact Rating (O-3): No data available.

Acute Aquatic Toxicity: No data available.

Degradability: No data available.

Log Bioconcentration Factor (BCF): No data available.

Log Octanol/Water Partition Coefficient: No data available.

#### **SECTION 13: DISPOSAL INFORMATION**

RCRA Hazardous Waste: No data available.

Waste Disposal: Disposal must be in accordance with standards **applicable** to generators of **hazardous** waste, 40 <u>CFR</u> 262, EPA Hazardous **Waste** number DOOl. A **100-pound** (CERCLA Section 103) Reportable Quantity.

#### SECTION 14 TRANSPORTATION INFORMATION

#### **Department of Transportation Hazard Classification:**

49 CFR 172.101, Nonflammable gas

Department of **Transportation** Labeling Requirements:

49 CFR 172.101 and Subpart E, Nonflammable gas and poison

Department of Transportation Packaging Requirements:

49 CFR 173.304; 49 CFR 173.314 and 49 CFR 173.315

**Exceptions: None** 

Final ruk on hazardous materials regulations (HMR, 49 <u>CFR</u> Parts 171-180), Docket numbers HM-181, HM-181A, HM-181B, HM-181C, HM-181D and HM-204. Effective date October 1, 1991. However, compliance with the regulations is authorized on and after January 1, 1991. (55 <u>FR</u> 52402, 12/21/90).

Except for explosives, inhalation hazards, and infectious substances, the effective date for hazard communication requirements is extended to October 1, 1993. (56 FR 47158. 09/18/91).

U.S. Department of Transportation Shipping Name-ID Number:

49 CFR 172.101, Chlorine-UN 1017

U.S. Department of Transportation Hazard Class or Division:

49 CFR 172.101, 2.3- Poisonous Gas

U.S. Department of Transportation Labeling Requirements:

49 CFR 172.101 and Subpart E, Poison Gas

U.S. Department of Transportation Packaging Authorizations:

**Exceptions: None** 

Non-Bulk Packaging: 49 CFR 173.304

Bulk Packaging: 49 CFR 173.314 and 49 CFR 173.315

#### **SECTION 14:** TRANSPORTATION INFORMATION (continued)

U.S. Department of Transportation Packaging Authorizations: 49 CFR 172.101

Passenger Aircraft or Railcar: h-bidden

Cargo Aircraft Only: Forbidden

#### **SECTION 15: REGULATORY INFORMATION**

TSCA Status: Y

Other Regulatory Information Available:

CERCLA section 103 (40 CFR 302.4): Yes 10 pounds RQ

SARA Section 302 (40 **CFR** 355.30): Yea 100 pounds TPQ

SARA Section 304 (40 CFR 355.40): Yea 10 pounds RQ

SARA Section 313 (40 **CFR** 372.65): Yes

OSHA Process Safety (29 CFR 1910.119): Yes1,500 pounds TQ

California Proposition 65: No

SARA Hazard Categories, SARA Sections 311/312 (40 CFR 370.21)

Acute Hazard: Yea

Chronic Hazard: No

Fire Hazard: No

Reactivity Hazard: No

Sudden Release Hazard: Yes

#### **SECTION 16: OTHER**

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Creation Date: 10/16/84 Revision Date: 12/30/93

Licensed to: HEHF

## APPENDIX E: RÉSUMÉS OF HAZOP STUDY TEAM

**Industrial** Hygiene, Chemical Safety

#### **Experience**

#### 15 years

- Performed surveys on a nationwide basis in manufacturing, petrochemical facilities, and
  offices to improve indoor air quality. Evaluated exposures to asbestos and fibrous glass
  fibers, wood dust, respirable silica, welding fumes, metals, and other airborne
  particulate. Monitored personal exposures to solvent vapors, sewer gases, plastic
  monomers and resins, carbon monoxide, and other gases and vapors.
- Conducted heat stress monitoring and surveying for ionizing and non-ionizing radiation hazards.
- Developed asbestos training programs for more than 1,000 workers. **Directed** bio-environmental engineering program for **Air National** Guard Base.
- Reviewed facilities engineering plans pertaining to industrial hygiene. Recommended corrections and/or designed ventilation systems at manufacturing facilities.

#### Education

B. S., Environmental Science, University of Michigan

#### Other

**Certified** Industrial Hygienist Certified Hazardous Waste Worker

Hazard Analysis Process Operator, Process Safety and Risk Management

#### Experience

#### 16 years

- Plant supervisor responsible for the operation of steam, water, process air, and sanitary sewer utilities of the Hanford 300-Area. Responsibilities include maintenance and operation of chlorination process equipment and the chlorine cylinder storage area. Assisted in development of the chlorine cylinder storage and handling facilities, chlorination process equipment, and operating procedures.
- Plant operator of steam, water, process air, and sanitary sewer utilities in the Hanford 300-Area. As plant operator, controlled chlorination system, including processing and chlorination of potable water, and sampling and testing of water in accordance with State of Washington code.

#### **Education**

U.S. Navy Basic Propulsion and Engineering School

U.S. Navy Boiler Technician "A" School

#### Other

State of Washington Group II Water Treatment Operator

Hazard and Risk Analysis

#### **Experience**

#### 22 years

- Experience in occupational safety, industrial hygiene, human factors, fire safety, and **safety** management.
- Consulted with numerous organizations on safety issues and processes. Assisted in program review and development and accident analysis. Performed safety process reviews and audits to determine general and chemical process hazards.
- Managed consultants and developed service programs to reduce accident frequency for the firms serviced. Managed training, industrial hygiene, and general safety programs for these consulting programs. other responsibilities included training, safety literature development, and performance management.
- . Developed preliminary hazard analyses **for** new and existing U.S. Department of Energy research facilities.

#### **Education**

- B. S., Physics, Oregon State University
- M. S., Industrial Engineering, Oregon State University

#### Other

Certified Safety Professional

Process Safety Management

#### **Experience**

#### 10 years

- U.S. Department of Energy, Occupational Safety and Health Manager. Responsible for development of technical guidance documents in occupational safety.
- DOE Program Manager. Responsible **for** development of tools **for** DOE-wide implementation of the Occupational Safety and Health Administration rule, 29 **CFR** 1910.119, "Process Safety Management of Highly Hazardous Chemicals."
- •OSHA, General Industry Compliance Assistance. As a safety engineer, responsible for development of the Special Emphasis Program, **PETROSEP**, which directed compliance personnel in conducting inspections at petrochemical facilities. Provided interpretation of OSHA standards and developed directives interpreting performance-based OSHA standards, Conducted chemical **plant** inspections assessing chemical process safety. Conducted workplace accident investigations involving chemical releases and explosions.
- West Virginia Department of Natural Resources, Division of Hazardous Waste Management. As a chemical engineer, reviewed Part B applications for Resource Conservation and Recovery Act facilities. Participated in the development of state hazardous waste management regulations.

#### **Education**

B. S., Chemical Engineering, Osmania University, Hyberabad, India

M. S., Chemical Engineering, Ohio State University

Process Hazard Anal ysis Leader, Process Safety and Risk Management

#### Experience

#### 20 years

- Hazard and operability **(HAZOP)** study leader **for** numerous facilities, including manufacturers of **sulfuric** acid, **oleum**, and liquid SO<sub>3</sub>; a hydrocarbon recovery system; startup and operating procedures **for** three refineries; a state-of-the-art hazardous waste disposal **facility**, for which accident scenarios were assessed **for** frequency and consequences; a batch-process catalyst manufacturing plant survey and upgrade; and an advanced absorption heat transfer system.
- Led a preliminary hazard analysis for the **design** of a hazardous waste processing plant. PHA addressed the locations of hazards and their relative risks. Planned and led a risk audit of a chemical process plant that used large quantities of hydrogen sulfide. The audit covered process components, operation, and maintenance, and onsite transportation. Led a risk assessment of a chemical pilot **plant** where temperature **control** was critical. Used **fault trees** to model system **failures** that **could** cause loss of temperature control.
- Author of numerous publications on hazard evaluation and **HAZOP** study procedures.
- Presented numerous seminars and workshops on risk assessment. Currently leads the American Institute of Chemical Engineers Center **for** Chemical Process Safety continuing education course, "Use of Hazard arid Operability Studies in Process Risk Management." This course has been presented to more than 1,200 engineers and 20 different companies.

#### **Education**

B. S., Electrical Engineering, University of Cincinnati

M. S., Engineering, University of Santa Clara

Mechanical Engineering, Risk Assessment, Human Factors

#### Experience

30 years

- Us. Department of Energy, Risk Assessment Team Manager. As Safety Analysis Division Director, **performed** oversight of DOE safety analyses, development of safety and risk policies, and review of reactor and non-reactor probabilistic risk assessments.
- Nuclear Regulatory Commission, Region 1, Technical Assistant. Provided technical support to regional management concerning inspection activities and risk-based applications. Inspection team leader on major probabilistic risk assessment-based inspections. Program manager of Calvert Cliff's and LaSalle PRAs.
- Design and safety specialist in space electric and nuclear applications at **Hittman** Associates, Inc.
- U.S. Atomic Energy Commission. Program manager for space electric component development, reactor core and shielding design, and major nuclear project construction.

#### **Education**

B. S., Nuclear Engineering, New York State Maritime College M. B.A., Engineering Management, George Washington University

#### Other

Certification, Oak Ridge School of Reactor Technology

Chemical Engineering, Hazard and Risk Analysis

#### Experience

#### 20 years

- Group Leader, Risk and Safety Analysis.
- Project manager for the **Liquified** Gaseous Fuels Release Prevention and Control Project.
- Project manager, task manager, and technical contributor to numerous risk and safety analyses of energy-related systems, including nuclear reactors and **fuel** cycle facilities, nuclear waste **facilities**, chemical waste facilities, and chemical facilities.
- Preparation of safety analysis reports for U.S. Department of Energy **nuclear** and chemical facilities at the **Hanford** Site.

#### **Education**

- M. S., Chemical Engineering, University of Washington
- B. S., Chemical Engineering, Carnegie Mellon University

#### Other

Registered Professional Engineer, Washington

Industrial Hygiene, Hazard and Risk Analysis

#### Experience

#### 22 years

- **Performed** risk and **safety** analyses for chemical operations in various U.S. Department of Energy facilities at the Hanford Site. Responsible for safety documentation of the new Pacific Northwest Laboratory Environmental and Molecular Sciences Laboratory.
- Developed an occupational health and safety program for the International Atomic Energy Agency Department of Safeguards.
- Senior Industrial Hygienist for PNL with a staff of 3,000.
- Regional Safety Manager **for** the U.S. Fish and Wildlife Service supporting managers of fish hatcheries and wildlife refuges in a six state region.
- System safety engineer at Headquarters, U.S. Army Test and Evaluation Command, and at two proving grounds. Supported safety test design and evaluation. Responsible for the resolution of technical occupational safety and health issues at the proving grounds.

#### Education

- M. E., Industrial Engineering (System Safety), Texas A&M University, 1974
- B. S., Industrial Engineering, University of Washington, 1971
- B. S., Mechanical Engineering, University of Washington, 1971

#### Other

Certified Safety Professional Certified Industrial Hygienist Professional Engineer in Safety Engineering in the State of California

Hazard Analysis, Process Engineer

#### Experience

#### 23 years

- Plant Engineer in the 300-Area Utilities and Effluent Treatment Plant, leading efforts in
  domestic and process sewer upgrades, installation of filter backwash pond and outfall,
  construction of filter plant chlorine storage facility, installation of new chlorinators and
  of treated effluent disposal system, replacement of ash sluice pond, and installation of
  metering manhole for the process sewer.
- Waste Water Plant Superintendent **for** Industrial and Domestic Treatment Plant of the City of Presser, Washington, including maintenance and operation of spray field and sewer system. Designed reviews of new filtration plant and waste water plant upgrade.
- Chief operator for the water treatment plant for the City of **Yakima**, Washington, including supervision of **influent**, grit, and rag removal; primary clarification centrifuge; primary and secondary digesters; trickling filters; activated sludge final clarification; chlorination; and spray field **for** industrial wastes.
- Operator and maintenance employee **for** the watershed of the City of The **Dalles**, Oregon, Waste Water Treatment Plant and Filter Plant. Participated in waste water plant construction, startup, and operation.

#### **Education**

Domestic and industrial waste water treatment training, Lim Benton Community College Work-related **classes** at Columbia Basin College

#### Other

State of Washington Group IV Waste Water Treatment Process Operator State of Washington Group II Waste Water Treatment Process Operator